INFRARED ABSORPTION AND DEBYE-WALLER FACTOR DUE TO

SUBSTITUTIONAL IMPURITY IN CUBIC CRYSTALS


A

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## ABSTRACT

The infrared absorption line shapes involving one phonon process have been obtained in cubic crystals containing substitutional impurities using thermodynamic Green's functions and Kubo formalism. With the aid of group theoretic arguments it is shown that only the totally symmetric or s-type one dimensional irreducible representation of the point group of the crystal contributes to the impurity vibration and hence, to the optical absorption. Conditions for occurence of inband resonant modes are investigated. An estimate is made of the change of nearest neighbour force constant in the case of $Li^6$ and $Li^7$ in KBr, based on the experimental data of Sievers and Takeno. A formula for the integrated absorption over all the modes is derived.

The expressions for the mean square displacement and velocity of the defect are obtained. The former was used to compute the Debye-Waller factors for $Fe^{57}$ in platinum, palladium and copper and using the available experimental data an estimate of the change of force constant is made in each case within the framework of the models studied.

# INTRODUCTION

The study of the effect of imperfections on the physical properties of crystalline solids is an important branch of solid state physics. All crystals in nature contain some defects or disorders. Presence of defects changes the physical properties of crystals in various ways. Point defects such as substitutional impurities, vacancies and interstitials etc. change the vibrational thermodynamic properties of solids by altering the frequency spectrum. The mechanical properties such as compressibility etc. are known to change due to the presence of higher dimensional defects such as dislocations (one dimensional defect), stacking faults (two dimensional defect) etc. This dissertation contains the results of a theoretical investigation of the effect of point defects on lattice infrared absorption and Mössbauer effect in cubic crystals.

In crystalline solids in the equilibrium configuration the atoms are arranged in a regular array called the 'lattice'. The electrostatic interaction between the ions and the electrons is mainly responsible for the binding energy of the solid. At finite temperatures the ions vibrate about their equilibrium positions. Owing to the smallness of the ratio between the electronic and nuclear masses, the velocities of the ions will be much

smaller than the velocities of the electrons. It is thus possible to assume that the electrons follow the nuclear motion adiabatically, i.e. the electrons at any time move as if the ions were fixed in their instantaneous positions. This adiabatic or Born-Oppenheimer approximation[1] implies a potential $V(\underline{R})$ which can describe the lattice vibrations.

For small vibrations the potential energy $V(\underline{R})$ can be expanded in a Taylor's series in terms of the displacements $\{\underline{U}\}$ of the ions from their equilibrium positions. For a Bravais crystal containing N atoms we have

$$V(\underline{R}) = V(\underline{R}_0) + \sum_{\underline{j},\alpha} A_\alpha(\underline{j}) u_\alpha(\underline{j}) + \tfrac{1}{2} \sum_{\substack{\underline{j},\alpha \\ \underline{j}',\beta}} A_{\alpha\beta}(\underline{j},\underline{j}') u_\alpha(\underline{j}) u_\beta(\underline{j}') + \cdots \quad (1.1)$$

where $V(\underline{R}_0)$ is the equilibrium potential energy of the crystal and

$$A_\alpha(\underline{j}) = \left[ \frac{\partial V(\underline{R})}{\partial u_\alpha(\underline{j})} \right]_{\underline{R} = \underline{R}_0} \quad (1.2a)$$

$$A_{\alpha\beta}(\underline{j},\underline{j}') = \left[ \frac{\partial^2 V(R)}{\partial u_\alpha(\underline{j}) \, \partial u_\beta(\underline{j}')} \right]_{\underline{R}=\underline{R}_0} \quad (1.2b)$$

$$\underline{R} = \underline{R}_0 + \underline{U} \quad (1.2c)$$

For harmonic solids the terms upto quadratic in $\underline{U}$ are retained. Higher order terms characterise the anharmonicity. In equilibrium configuration the net force acting on any

atom is zero, hence the Hamiltonian of the crystal in the harmonic approximation is written as

$$H = \sum_{j,\alpha} \frac{p_\alpha^2(j)}{2M_j} + \frac{1}{2}\sum_{\substack{j,\alpha \\ j,\beta}} A_{\alpha\beta}(j,j) \, u_\alpha(j) \, u_\beta(j) \qquad (1.3)$$

where $M_j$ is the mass of the $j$-th atom. The harmonic force constants $A_{\alpha\beta}(j,j)$ reflect the physical symmetries of the lattice. The general relationships among the force constants are discussed in the standard books on the subject.[2-4]

In harmonic approximation the system of coupled oscillators can be solved exactly with the aid of normal co-ordinate transformation which transforms the system of coupled oscillators into a set of independent oscillators called normal modes, each having its characteristic frequency of vibration. The translational symmetry of the crystal leads to a normal mode being in the form of a travelling plane wave, characterized by a wave vector $\underline{k}$ and frequency $\omega_j(\underline{k})$, j being the branch index. The motion of any atom in the lattice is due to the superposition of these normal modes. Since the total number of atoms in the crystal is very large, the frequencies form quasi-continuous bands. This description of solids in the harmonic approximation explains many of the properties, such as the low temperature specific heat (Debye $T^3$ law), infrared reflectivity of ionic crystals, etc..

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In the language of quantum theory the lattice vibrations can be treated as a field and quantization[5] of such a field results in what are known as 'phonons'. The lattice vibrational quanta or phonons have no widths in the harmonic approximation and hence have infinitely long life time, but inclusion of anharmonic effects brings about interaction among the phonons leading to a finite life time which plays a vital role in lattice thermal conductivity, thermal expansion, shape of fundamental absorption line in ionic crystals and a host of other properties. The phonon description of lattice vibrations is closely related to the classical normal mode analysis, because the independent normal modes get coupled in presence of the non-linear terms in the crystal potential energy. One switches over to the phonon picture by expressing the normal modes in terms of annihilation and creation operators. However, for higher order processes the phonon description is more suitable as there exist convenient tools such as many-particle Green's functions and diagrammatic techniques[6] of the perturbation theory for the many-body problem. Besides the phonon-phonon interaction arising out of anharmonicity, interaction of phonons with other elementary excitations also adds to their life time.

The interaction among the phonons is also brought about by the defects which are present in most of the solids. The pioneering work in this field was that of Lifshitz[7-10]

who had evaluated the perturbed frequencies and normal modes in an imperfect crystal and discussed the other physical properties of such a crystal. Montroll and Potts[11,12] gave a method of attack for this problem based on the use of Green's function of difference operators, and they also app- lied it to some idealized models of lattices with impurities. Montroll[13] et al , Tanaka and Yamahuzi,[14] Mahanty, Maradudin and Weiss[15,16] and the Russian school lead by Lifshitz[17] have studied the effect of impurities on vibrational thermodynamic properties which are additive functions of the normal mode frequencies. Rubin[18] has studied the detailed dynamics of an impurity atom in a lattice.

Besides the change in the normal mode frequencies, the localized nature of the impurity perturbation depending on its strength (mass of the impurity and its interaction with the host) gives rise to two interesting features. New modes of vibration, are often generated having frequencies above the maximum frequency of the unperturbed crystal, accompanied by a certain change in the density of states within the bands. These modes are called 'localized modes' as the displacement amplitude of such a mode falls off with increasing distance from the impurity site. In harmonic solids such a high frequency mode cannot decay into the band and has a δ-function line shape. However, anharmonicity[19] and impurity-impurity interaction[20,21] leads to a finite life time for this mode

and hence a well defined shape to the line. Secondly, under suitable conditions an impurity does not produce a local mode, but a significant redistribution of levels within the bands, occurs in such a way that in the neighbourhood of a certain frequency a marked enhancement in the density of states takes place, such a peaking up in the density of states is known as a 'resonance' or 'quasi-localized' state. Due to the presence of a large number of states in the vicinity this mode decays with a finite life time even in the harmonic approximation. Localized modes can also occur in the forbidden regions between the acoustic and optic branches of the frequency spectra in ionic crystals. These modes are called the gap modes.

The existence of localized modes in solids was known from the work of Lifshitz, though the possibility of occurence of inband resonant modes was over-looked in the earlier stages of the work. Brout and Visscher,[22] Kagan and Iosilevskii[23] and Takeno[24] independently had pointed out this possibility theoretically. Brout and Visscher were able to calculate the frequency of this low lying mode caused by a heavy isotopic impurity (impurity host interaction remains unchanged) in Debye model as

$$(\omega_r/\omega_m)^2 \sim \frac{1}{3(\frac{\Delta M}{M})} \qquad (1.4)$$

where $\Delta M = M' - M =$ mass of the impurity — mass of the host atom

$\omega_m$ = Debye cut off frequency.

The width of this mode was calculated in detail.

Koster and Slater[25,26] had considered the effect of an impurity atom which produces a different potential at the impurity site, on the electron energy spectrum of a metal. The problem of scattering of spin waves due to impurities in ferromagnets was discussed by Wolfram and Callaway[27,28] and Takeno[29] independently. There exists a great deal of similarity in the problems of impurity affecting the electrons, the phonons and the magnons in solids which makes it possible to treat them on the same mathematical footing. This aspect has been discussed by Izyumov[30]

The problem of lattice dynamics of imperfect crystals involves the study of the above aspects both theoretically and experimentally. Both the localised and resonant modes were first predicted theoretically. With the availability of experimental techniques in the measurement of low temperature thermal conductivity, specific heat, elastic and inelastic scattering of neutrons, lattice infrared absorption and Mossbauer effect one can go into the details of defect vibrations. Here we briefly outline the various experimental methods for studying the impurity activated modes.

In case of insulators the thermal resistance is produced due to the scattering[31,32] of lattice vibrations or

phonons. Although the impurities are known to scatter phonons, the main contribution to thermal resistance at high temperatures comes from the phonon-phonon scattering due to the anharmonic terms in the crystal potential energy. However, at very low temperatures the impurity contribution sometimes becomes much more pronounced, so as to be observed distinctly. Pohl[33] first observed a dip in the low temperature region of the thermal conductivity curve when plotted against temperature for potassium chloride crystal containing a small concentration of potassium nitrite. The usual Raleigh type of scattering[34,35] of phonons at low frequencies could not explain the result and Pohl reproduced the dip by assuming a resonant form for the inverse relaxation time. Subsequently the effect was confirmed by a series of measurements of the thermal conductivity of KCl doped with KI, NaCl, and $CaCl_2$ by Walker and Pohl[36]

The occurence of Brout-Visscher resonance due to a heavy mass defect or softening of impurity-host interaction led to the conclusion that the resonant scattering of phonons at low frequency which in temperature scale corresponds to such a low temperature was responsible for the thermal conductivity dip. This was the first experimental evidence for the occurence of inband resonant mode in solids. In case of a molecular defect like $NO_2^-$ and $CN^-$ the resonance origin is due to the internal degrees of freedom of the molecular

vibrations whose frequency lies embedded in the phonon spectrum. The molecular impurity problem was discussed theoretically by Wagner[37-39] who introduced molecular Green's functions characterising the new degrees of freedom and solved the resulting set of coupled equations for scattering and localized modes.

Since the defect changes drastically the frequency spectrum, the properties such as specific heat which directly depends on it should show up the impurity mode[40] In fact, the low frequency resonant mode which produced a marked enhancement in the specific heat at low temperature was detected by Lehman[41] et al and Panova and Samoilov[42] in Mg containing Pb and Cd as impurities.

In perfect crystals, the inelastic coherent and incoherrent scattering of neutrons involving one phonon process directly reveals the dispersion (frequency wave vector dependence) relation and frequency spectrum respectively in cubic crystals. The experimental detection of the low frequency resonant mode was made by Møller and Mackintosh[43] in chromium mixed with tungsten and by Svensson, Brockhouse and Rowe[44] in copper doped with gold. The first group of experimenteers also observed a temperature independent shift (non-anharmonic) of the resonant mode. Such a shift which arises due to impurity-impurity interaction was calculated by Elliott and Maradudin[45] by considering many isotopic

impurities distributed at random in the crystal. The result could not agree quàntitatively with the above experiments, although there was a qualitative agreement. Recently Behera and Deo[46] extended the theory by including the change in impurity host interaction and using diagrammatic method in a rather phenomenological way. To our knowledge the discrepancy between the theoretical calculation and result obtained from the experiment still exists. Elliott and Taylor[47] and Taylor[48] discussed the solution of Dyson equation for many impurities in co-ordinate space. Recently Takeno[49] obtained a formal solution in case of an extended defects (including change of impurity host force constants). Although these are improvements over the previous theories, the results are far from satisfactory for higher concentrations of impurities.

The existence of localized modes were observed as peaks in the energy distribution of neutrons scattered inelastically and incoherrently in palladium containing nickel as light impurities by Mozer, Otnes and Myers,[50]

Interaction of electromagnetic radiation with matter is by far one of the oldest and fundamental branches in physics. In crystalline solids this interaction yields information about its structure and throws light on mechanisms of various physical processes. The existence of a non-vanishing dipole moment in harmonic crystals corresponding to the transverse optic mode of zero wave-vector $(\omega)_{TO}$ is

known to cause Reststrahln phenomena in ionic crystals. As regards lattice vibrations whose frequencies extend from zero to a certain maximum value which lies in the far infrared region of electromagnetic spectrum, the optical absorption experiments provide perhaps the most direct method available at present, although the experimental difficulties of far infrared spectroscopy are substantial.

Schaefer[51] observed for the first time in 1960 a high frequency lattice mode in the infrared in alkali halide crystals containing hydride ions as impurities. This is known as U-center and is caused by the appearance of an infrared active local mode outside the maximum frequency of the crystal. Schaefer also observed sidebands on both sides of the main U-center band. The frequency of the U-center was calculated by Wallis and Maradudin,[52] and by Takeno[53] et al , using a nearest neighbour force model for the host crystal and obtained a good agreement with the experiment in the mass defect approximation. However, when long range electrostatic forces are taken into account the agreement becomes poor. More realistic calculation by Jaswal and Montgomery[54] using regid ion and deformation dipole models, and by Fieschi, Nardelli, and Terzi[55,56] using a shell model showed that a 50% reduction of nearest neighbour force constant is required to fit the data. Mirlin and Reshina[57] and Fritz[58,59] have studied the details of the wing structure and the temperature dependence

of the main band. Fritz observed a strong temperature dep-
endent peak with half width decreasing as $T^2$ at room tempe-
ratures and he ascribed this and the appearance of the side
bands to the interaction of the local mode with the band
modes through the anharmonicity of the crystal potential
energy. Timusk and Klein[60-61] have developed a theory to
explain the side band structure in terms of the anharmonic
coupling of $H^-$ ion to its nearest neighbours. Nguyen[62] has
performed a similar calculation including both the anharmonic
and second order electric dipole moment interaction. The
later result showed that the dominant factor arises due to
anharmonicity. Experimental and theoretical investigations
were also carried out by Mitra and Brada[63] whose results were
similar to that of earlier observations.

Balkanski and Nazarewicz,[64,65] and Angress[66] et al
observed infrared active local modes and band modes, acti-
vated by the impurities like boron and phosphorus in silicon.
Montgomery and Hardy[67] studied the isotopic variations of
dispersion frequency in mixed alkali halides.

As regards the inband resonant modes in ionic cry-
stals are concerned, the first observations were those of
Sievers[68] in potassium halides containing silver ions as
impurities. These resonances lie in the low frequency region
of the acoustic band ($100 cm^{-1}$ to $10 cm^{-1}$) and arise due to
the heavy mass of the silver ion. He in collaboration with

Takeno[69] could detect a very low lying sharp impurity mode for very light impurities like $Li^{6,7}$ in KBr. In all these cases the absorption frequency decreases slightly and half-width increases with the rise of temperature.[70] Their observation gave an impetus in understanding the configuration of small ions like Li in alkali halide crystals and this will be discussed in Chapter IV. Localized modes inside the forbidden region or the gap modes[71] were also observed by Sievers and his co-workers in KI due to $Cl^-$ and $Br^-$.

The existence of molecular impurity centers in alkali halides were known from the thermal conductivity measurements.[33] However, thermal conductivity results alone cannot furnish all the informations regarding the internal degrees of freedom like free rotations, hindered rotations and tunneling etc.. The molecular modes are infrared active and show up in the absorption experiments. The energy levels of molecules and transition from hindered rotation to free rotation with increase of temperature were studied by Seward, Narayanamurti and Pohl.[72-74] A somewhat clearer picture of molecular vibrations in solids emerges from the combined study of both these properties.

Infrared measurements were also carried out in rare gas crystals by Jones and Woodfine[75] who measured the one phonon absorption spectra of solid argon containing nearly 2 % of krypton or xenon (neutral impurities). Very recently

Klein and Macdonald[76] detected the isotopic absorption spec-
trum in NaCl and LiF crystals. The natural $Cl^{35,37}$ isotopes
acting as simple mass defects result in absorption in the
acoustic band and yield information about the phonon frequen-
cies at critical points. This is the first observation of
isotope induced band mode absorption in alkali halides to our
knowledge.

The theoretical work in this field is mainly confi-
ned to the isotopic impurity case or the so called mass defect
approximation (MDA). In this approximation an expression for
absorption co-efficient due to charged impurities in otherwise
uncharged host was obtained by Dawber and Elliott.[77] In ionic
crystals the notables are the work of Hardy,[78] Gunther[79] and
Maradudin.[19] Maradudin has given a general formula for the
absorption co-efficient using the propagator technique.
Recently the case of an extended impurity (involving a change
of mass as well as nearest neighbour force constant) was
discussed by Patnaik and Mahanty,[80] Benedek and Nardelli[81]
and Takeno.[82]

Before discussing any further regarding the defect-
activated absorption we will briefly discuss the mechanism of
interaction between the crystal and the radiation field. In
the process of absorption, emission or scattering of electro-
magnetic radiation, the quantum mechanical description involves
two states of the crystal namely the initial and the final

state. Here we assume that both these states do not take into account the motion of electron inside the ions or atoms. In otherwords we exclude from our consideration the electronic transitions. Hence the infrared absorption is concerned with the process where the initial state is the crystal in the ground state and an incident photon, whereas the final state is an excited state of the crystal with one or more phonons. This process can take place if the crystal possesses dipole moment. Like the potential energy, the dipole moment depends on the nuclear co-ordinates and hence can be expanded in terms of their displacements from the equilibrium position in a Taylor's series as

$$M_\alpha(\underline{R}) = M_\alpha^0 + \sum_{j,\beta} e_j^{\alpha\beta} u_\beta(j) + \sum_{\substack{j,\beta \\ j',\gamma}} e_{jj'}^{\alpha\beta\gamma} u_\beta(j) u_\gamma(j') + \cdots \tag{1.5}$$

where $M_\alpha(\underline{R})$ = $\alpha$- cartesian component of the dipole moment of the crystal,

and

$$e_j^{\alpha\beta} = \left[ \frac{\partial M_\alpha(\underline{R})}{\partial u_\beta(j)} \right]_{\underline{R} = \underline{R}_0} , \tag{1.6a}$$

$$e_{jj'}^{\alpha\beta\gamma} = \left[ \frac{\partial^2 M_\alpha(\underline{R})}{\partial u_\beta(j) \partial u_\gamma(j')} \right]_{\underline{R} = \underline{R}_0} \tag{1.6b}$$

$\{ e_j^{\alpha\beta} \}$ and $\{ e_{jj'}^{\alpha\beta\gamma} \}$ satisfy conditions[2] similar to these of force constants. For cubic crystals $M_\alpha(\underline{R})$ is isotropic and

$M_\alpha^O$ which represents a permanent dipole moment does not occur, hence we can write

$$M_\alpha(\underline{R}) = \sum_j e_j u_\alpha(j) + \sum_{jj'} e_{jj'} u_\alpha(j) u_\alpha(j') + \ldots$$

$$(1.7)$$

The co-efficient $e_j$ represents the 'effective charge' of the $j^{th}$ atom and the term containing it is the linear moment. The co-efficients $e_{jj}$ which are involved in the second order moment, determine the effective charge of $j^{th}$ atom which is produced by the displacement of $j^{th}$ atom. In ionic crystals the first order dipolemoment exists whereas the effective charge is zero for homopolar crystals such as those having diamond structure. The second and higher order moments exist for both polar and non polar crystals.

For polar crystals the existence of the linear moment leads to one phonon absorption process only at one frequency $(\omega_{TO})$ with a $\delta$-function shape. This is the well known fundamental absorption line, sometimes called the Reststrahl absorption. Although there is no one phonon absorption in crystals having diamond structure, they do exhibit a weak well-defined absorption spectrum involving two or more phonons due to higher order moments. It had been first proposed by Lax and Burstein[83] that the presence of charged defects in homopolar crystals will make the whole range of lattice modes optically active. In ionic crystals the defect destroys the

translational symmetry and relaxes the selection rules. However, it is not necessary to introduce charged substitutional impurities, as any atom becomes polarised by distortions induced by the vibrations of the neighbouring atoms due to their unequal electron affinity. The induced first order dipole moment interacts with the electromagnetic radiation to give optical absorption, the experimental evidence of such absorption spectra were observed by Jones and Wood-fine[75] in rare gas crystals as mentioned earlier and by Newman and Willis[84] in silicon containing carbon as impurities.

Theoretical calculation of effective charges were made by Szigeti[85,86] in homopolar crystals and by Hartman and Elliott[87] in rare gas crystals. Before closing the formal discussion on the photon-phonon interaction, it may be pointed out that induced enelastic scattering of light by phonons (Raman effect) takes place in ionic crystals due to the presence of a defect which changes the electronic polarizability[88] of the crystal in first order.

After the discovery of Mossbauer[89] effect i.e. the recoil free emission or absorption of γ-rays in crystals, it became a very useful tool for the study of defect dynamics. There are three dynamical quantities of interest in connection with the resonant absorption or emission of γ-rays in crystals. The 'zero phonon' process in which the crystal

remains in the same state after the absorption (or emission) of photon is known as Móssbauer effect. The quantum mechanical probability for occurence of such process is given by the Debye-Waller factor which depends on the mean square value of the displacement of the emitting nucleus. The second quantity of interest is the shift (temperature dependent) of the position of the zero phonon line due to an increase in the vibrational energy of the crystal, because of decrease in mass of the emitting nucleus as a consequence of the relativistic equivalence of mass and energy. This is known as second order 'Doppler shift' and is proportional to mean square velocity. The third quantity relates to 'one phonon process' in which the $\gamma$-rays photon is absorbed with a change of energy of the crystal by one quantum of vibration. This gives information about the frequency distribution function of the host crystal when the resonant nucleus does not differ from the atom it replaces (true isotopic impurity case). The resonant mode or local mode if present will show up in one phonon process. The literature in this field is very vast. The works of visscher,[90] Maradudin,[91] and Lehman and DeWames[92] deal with the defect dynamics associated with the Mossbauer effect. Most of the earlier papers on the experimental and theoretical status are discussed by Fraunfelder.[93]

The brief review given here is not intended to be exhaustive. Detailed reviews of the experimental and theore-

tical situation are available in a number of review articles.[19,94-99]

The present thesis is mainly concerned with the theoretical investigations of impurity activated infrared absorption due to a charged substitutional impurity in an otherwise uncharged host, and by an impurity in ionic crystal taking into account the change of mass as well as the nearest neighbour force constant in some solvable models of cubic crystals. Expressions for the mean square velocity and displacement of the impurity are obtained, and the results compared with the available experimental data. A brief summary of the thesis is as follows:

In Chapter II we will discuss the mathematical formalism that is to be used. The double time temperature dependent Green's functions are discussed in general without assuming any specific form of the impurity potential. Expressions for the displacement and velocity co-relations functions are obtained in terms of the above Green's functions. We use the Kubo formula to study the response of the system to an external time dependent perturbation like that due to incident electromagnetic radiation and a formula for optical absorption (Power absorption) is derived. A sum rule for the total integrated absorption including the band and localized modes is obtained and applied to the case of charged impurities and impurities in ionic crystals.

Chapter III deals with the absorption line shapes of charged impurities in simple cubic, body centered cubic and face-centered cubic crystals. The symmetry properties of the defect lattice is taken into account to decompose the resonant denominator into various factors representing the different irreducible representations of the point group., By group theoretical argument it is proved that only the totally symmetric or s-wave mode is infrared active. For understanding the low frequency mode a Deybe model is employed to obtain expression for the frequency of resonant mode and its halfwidth.

In Chapter IV infrared absorption in ionic crystals is considered. The model of ionic lattice is taken as a simple cubic lattice having alternatively positive and negative charges associated with the two different masses. Using the $\hat{M}$ transformation, which makes it a simple cubic lattice with an effective mass, the absorption line shape formula is discussed. The partioned forms of the perturbation and Green's function matrix are employed to sum over all the lattice sites. The absorption due to impurity is being separated from that of the host crystals. The results are compared with the experimental data of Sievers and Takeno. An estimation for the change of nearest neighbour interaction is made.

The mean square displacement and velocity are derived

for an impurity in Chapter V. An estimation of impurity host nearest neighbour force constant is made by fitting the theory to the experimental measurements of Debye Waller factor for $Fe^{57}$ in Pt, Pd and Cu lattices. In all these models a good fit to the experiment is obtained for a wide range of temperatures. A series expansion formula is derived for the mean square displacement which give also the correct fit.

In the concluding chapter the results of the investigation are summarised. The limitations of the theory is also discussed.

# CHAPTER II

## GREEN'S FUNCTION FORMALISM AND EXPRESSION FOR POWER ABSORPTION

### 2.1 General Formalism

It has been already pointed out that the entire solid from the point of view of lattice vibrations in harmonic approximation can be considered as an assembly of phonons. Hence the study of the vibrational properties of solids is essentially a many-body problem. The defects bring about interaction among the phonons and scattering takes place. Many formalisms were developed to treat such problems. The usual perturbation theory is not applicable to the study of localized modes. The defect problem is exactly solvable in harmonic approximation by making use of the classical equations of motion of the lattice and the Green's function technique devised by Lifshitz[10], Montroll and Potts[11]. The same problem can also be solved by quantizing the lattice vibrational field and then using the Green's function technique as prescribed by quantum field theory. However, both the methods are equivalent for the assembly of harmonic oscillators.

Here we use the method of the double time thermodynamic Green's function which has already been applied successfully and extensively for a variety of interacting systems. But the Hamiltonian for the lattice vibrations and hence the Green's functions are expressed in terms of the space co-ordinates rather than in the momentum space. In this form, the displacement and velocity correlation of

any two atoms can be expressed directly in terms of their Green's functions.

In literature there exist many reviews and texts on these Green's function formalism. We shall follow closely the review written by Zubarev[100]. There are three different types of Green's functions defined in terms of the average value of the T product of the operators, namely the causal, the advanced, and the retarded. We use only the retarded Green's function defined as

$$G(t,t') = \langle\langle A(t), B(t) \rangle\rangle = - i\Theta(t-t')\langle[A(t), B(t')]\rangle$$

(2.1)

where $A(t)$ and $B(t')$ are any two Heisenberg operators i.e.

$$A(t) = e^{iHt} A(o)e^{-iHt}$$

(2.2)

(a system of units in which $\hbar = 1$). H is the Hamiltonian of the system. The square bracket denotes the commutator

$$[A,B] = AB - BA$$

(2.3)

and $\Theta(t-t')$ is the Heaviside step function,

$$(t-t') = 0 \quad \text{for} \quad t > t'$$
$$= 1 \quad \text{for} \quad t < t'$$

(2.4)

The angular bracket denotes the ensumble average, i.e. for any operator A,

$$\langle A \rangle = \text{Tr } e^{-\beta H}A/\text{Tr } e^{-\beta H}$$

(2.5)

where $\beta = (k_B T)^{-1}$, $k_B$ being the Boltzman constant and T is the temperature of the system. The equation of motion obeyed

by the operator A is

$$i \frac{dA}{dt} = [A,H] \qquad (2.6)$$

Differentiating equation(2.1) with respect to t we obtain the equation of motion for the Green's function as,

$$i \frac{dG}{dt} = \delta(t-t') \langle [A(t), B(t')] \rangle + \langle\langle [A(t),H], B(t') \rangle\rangle . \qquad (2.7)$$

The second term in the above equation is another Green's function which is generally of higher order (involving more number of operators) than the original one. The usual way is to write the equation of motion of that Green's function which in its turns leads to a hierarchy of coupled equations. To solve this set of never ending equations one has to decouple the Green's function at a certain stage. There are no set rules which will decide this termination, but one has to make suitable approximation taking into consideration the physical situation. But in case of the defects lattice problem, the second Green's function is of the same order as that of the original one and its equation of motion yields the first Green's function. Hence one has to solve the resulting coupled equations simultaneously.

Let $G(\omega')$ be the Fourier transform of the Green's function $G(t-t')$, then

$$G(t-t) = \int_{-\infty}^{+\infty} e^{-i\omega(t-t)} G(\omega) \, d\omega , \qquad (2.8a)$$

and

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega(t-t')} G(t-t') \, d(t-t') . \qquad (2.8b)$$

The physical quantities of interest in many problems are the time correlation functions defined as

$$F_{BA}(t,t') = \langle B(t') A(t) \rangle . \tag{2.9a}$$

$$F_{AB}(t,t') = \langle A(t) B(t') \rangle . \tag{2.9b}$$

Equal time correlation functions are called the auto-correlation functions and they give the average value of the product of the operators. One can express the correlation functions in terms of the spectral density function $J(\omega)$

$$F_{BA}(t-t') = \int_{-\infty}^{+\infty} d\omega\, J(\omega)\, e^{-i\omega(t-t')}, \tag{2.10a}$$

$$F_{AB}(t-t') = \int_{-\infty}^{+\infty} d\omega\, e^{\beta\omega}\, J(\omega)\, e^{-i\omega(t-t')}. \tag{2.10b}$$

where

$$G(\omega+i\varepsilon) - G(\omega-i\varepsilon) = -i\,(e^{\beta\omega}-1)\, J(\omega), \tag{2.11}$$

and $\varepsilon \to 0$ is implied.

The above expression relating the Green's function and the spectral density function is important. Once the retarded Green's function is known, the spectral density function can be obtained and then taking the Fourier transform one can get the expressions for various correlation functions at all times and at all temperatures.

## § 2.2 Linear Response Theory And Kubo Formula

Kubo has given an elegant formulation of the problem[101,102] of reaction of an external perturbation on a quantum mechanical

system while discussing transport phenomena like the elect-rical and thermal conductivity, Peltier effect etc. in terms of the time correlation functions of the respective currents. The theory is based on the assumption that the response of the system is linear to the external perturbation (i.e. elec-tric field in case of electrical conductivity etc.). The higher or the nonlinear terms are neglected in the above analysis, but they are important in the theory of phenomena which arise due to non-linearity.

Let us consider a system with time independent Hamil-tonian H. A perturbation $H_I^t$ which depends on time explicitly has been switched on at $t = -\infty$, when the system was in ther-mal equilibrium. Now the system is described by the Hamilto-nian

$$H' = H + H_I^t . \qquad (2.12)$$

The ensemble average of expectation value of any operator A is given by

$$\langle A \rangle = \mathrm{Tr}( \rho(t)A) \qquad (2.13)$$

where $\rho(t)$ is the density matrix representing the ensemble and satisfy the following equation

$$i \frac{d}{dt} \rho(t) = [H', \rho(t)] = [H+H_I^t, \rho(t)] . \qquad (2.14)$$

The above equation is to be solved under the initial condition

$$\rho(-\infty) = \rho = e^{-\beta H} / \mathrm{Tr}\, e^{-\beta H}, \qquad (2.15)$$

to the first order of perturbation, i.e.

$$\rho(t) = \rho + \Delta\rho(t) \tag{2.16a}$$

$$\Delta\rho(t) = 0 \text{ for } t = -\infty. \tag{2.16b}$$

Restricting the solution upto the linear term in the external perturbation and by making use of the initial condition the change in the density matrix is obtained as

$$\Delta\rho(t) = -i \int_{-\infty}^{t} e^{iH(t-t')} [H_I^{t'}, \rho] e^{-iH(t-t')} dt. \tag{2.17}$$

Now the average value of any operator A is given by

$$A = \text{Tr} ((\rho + \Delta\rho(t))A)$$

$$= A_0 + i \int_{-\infty}^{+\infty} \langle\langle A(t), H_I^{t'}(t') \rangle\rangle \, dt. \tag{2.18}$$

This expression gives the response of the system to the external perturbation in terms of the retarded Green's function.

## § 2.3 Electrical Conductivity

The crystal interacts with the electric field of the electromagnetic radiation through its dipole moment. Let the electric field $\underline{E}(t)$ of radiation be uniform throughout the entire space and vary sinusoidally with time, then

$$\underline{E}(t) = \underline{E} \cos \omega t \tag{2.19}$$

The corresponding interaction Hamiltonian is

$$H_I^t(t) = -\underline{M} \cdot \underline{E}(t) = -\sum_j e_j \underline{E} \cdot \underline{u}(j,t) \cos\omega t \, e^{\varepsilon t}. \tag{2.20}$$

where $\varepsilon$ is a small positive infinitesimal quantity indicating

the fact that the interaction was switched on at $t = -\infty$.

Under the interaction there arises an electric current and if one considers a unit volume of the crystal, the expectation value of the current density operator becomes

$$\langle J_\alpha(t) \rangle = \int_{-\infty}^{+\infty} \langle\langle J_\alpha(t), H_I^t(t') \rangle\rangle \, dt' . \qquad (2.21)$$

where

$$H_I^t(t) = H_I(t) \cos \omega t \, e^{\varepsilon t} , \qquad (2.22a)$$

$$J_\alpha(t) = \sum_j e_j \, \dot{u}_\alpha(j,t) , \qquad (2.22b)$$

with

$$H_I(t) = - \sum_{j,\alpha} e_j \, E_\alpha \, u_\alpha(j,t) . \qquad (2.22c)$$

Integrating by parts and using equation (2.22a) this reduces to

$$\langle J_\alpha(t) \rangle = - \operatorname{Re} \left\{ \langle [J_\alpha(t), H_I(t)] \rangle \frac{e^{(i\omega+\varepsilon)t}}{\omega - i\varepsilon} \right.$$

$$\left. + \int_{-\infty}^{+\infty} \langle\langle J_\alpha(t), \dot{H}_I(t) \rangle\rangle \frac{e^{(i\omega+\varepsilon)t}}{i\omega + \varepsilon} \, dt \right. \qquad (2.23)$$

The first term involves a commutator at equal time and is evaluated with the help of the usual relation.

$$[u_\alpha(j), u_\beta(j')] = \frac{i}{M_j} \delta_{\alpha\beta} \delta_{jj'} , \qquad (2.24a)$$

and

$$[u_\alpha(j), u_\beta(j')] = [\dot{u}_\alpha(j), \dot{u}_\beta(j)] = 0 . \qquad (2.24b)$$

Since

$$\dot{H}_I(t) = - \sum_{j,\alpha} e_j \, E_\alpha \, \dot{u}_\alpha(j,t) = - \sum_\alpha E_\alpha J_\alpha(t), \qquad (2.25)$$

equation (2.23) is rewritten as

$$\langle J_\alpha(t) \rangle = \text{Re} \sum_{?} \sigma_{\alpha\beta}(\omega) \, E_\beta \, e^{(i\omega + \varepsilon)t}. \qquad (2.26)$$

where the element of the conductivity tensor is given by

$$\sigma_{\alpha\beta}(\omega) = -\frac{i}{\omega} \sum_j \frac{e_j^2}{M_j} \delta_{\alpha\beta} + \int_{-\infty}^{+\infty} \langle\langle J_\alpha(0), J_\beta(t') \rangle\rangle$$

$$\frac{e^{(i\omega + \varepsilon)t'}}{i\omega + \varepsilon} \, dt'. \qquad (2.27)$$

The first term in the above expression corresponds to the electrical conductivity of a system of free charges. The conductivity tensor can also be expressed in terms of the time correlation of currents. However, it is expressed here in terms of the retarded Green's function directly. For convenience we define the velocity Green's function which is related to current Green's function by a multiplying factor and is similar to that of Elliott and Taylor,[103]

$$F_{\alpha\beta}(j,j';t) = (M_j M_j)^{\frac{1}{2}} \langle\langle u_\alpha(j,0), u_\beta(j',t) \rangle\rangle. \qquad (2.28)$$

In terms of its Fourier transform the conductivity tensor is expressed as

$$\sigma_{\alpha\beta}(\omega) = -\frac{i}{\omega} \sum_j \frac{e_j^2}{M_j} \delta_{\alpha\beta} + 2\pi \sum_{j,j'} \frac{e_j e_{j'}}{(M_j M_j)^{\frac{1}{2}}} \frac{F_{\alpha\beta}(j,j';\omega)}{\omega + i\varepsilon}. \qquad (2.29)$$

## § 2.4 Green's Functions And Correlation Functions Of The Lattice

In order to calculate the lattice electrical conductivity and electric current density etc. the knowledge of the lattice Green's functions is required. The expression for the Green's

function is obtained by writing down the equation of motion
of the Green's function as defined by the equation(2.28). i.e.

$$i \frac{d}{dt} F_{\alpha\beta}(\underline{j},\underline{j}';t) = - (M_{\underline{j}}M_{\underline{j}'}^{-1})^{\frac{1}{2}} \sum_{\eta,\gamma} A_{\alpha\gamma}(\underline{j},\underline{n}) \langle\!\langle u_{\alpha}(\underline{j},0),u_{\delta}(\underline{n},t)\rangle\!\rangle$$

(2.30)

Differentiating once again

$$\frac{d^2}{dt^2} F_{\alpha\beta}(\underline{j},\underline{j}';t) = - \delta(-t) \frac{A_{\alpha\beta}(\underline{j},\underline{j}')}{(M_{\underline{j}}M_{\underline{j}'})^{\frac{1}{2}}} - \sum_{\eta,\gamma} F_{\alpha\gamma}(\underline{j},\underline{n};t) \frac{A_{\gamma\beta}(\underline{n},\underline{j})}{(M_{\underline{n}}M_{\underline{j}})^{\frac{1}{2}}}$$

(2.31)

Here we have used the commutation relations as given by equat-
ions(2.24) and the lattice Hamiltonian as defined in Chapter I.
The above equation can be solved by matrix inversion method.
In matrix form, this and the defining equation(2.28) are writ-
ten respectively as

$$\frac{d^2}{dt^2} \hat{F} = - \delta(-t) \hat{D} - \hat{F}\hat{D} \quad , $$

(2.32)

and

$$\hat{F}(t) = \hat{M}^{\frac{1}{2}} \langle\!\langle \dot{\underline{U}}(0), \dot{\underline{U}}(t)\rangle\!\rangle \hat{M}^{\frac{1}{2}} .$$

(2.33)

The cap denotes the matrix. $\underline{U}(t)$ is the 3N dimensional vector
whose $(\alpha,\underline{m})$ element denotes the $\alpha$-component of the velocity of
the $\underline{m}^{th}$ atom.

where $\qquad \hat{D} = \hat{M}^{-\frac{1}{2}} \hat{A} \hat{M}^{-\frac{1}{2}},$

(2.34a)

and hence $D^0 = \hat{M}^{0-\frac{1}{2}} \hat{A}^0 \hat{M}^{0-\frac{1}{2}},$

(2.34b)

The matrices $\hat{D}$, $\hat{D}^0$, $\hat{M}$ and $\hat{M}^0$ are of 3N dimensions. $\hat{A}$ is the harmonic force constant matrix and $\hat{M}$ is the diagonal mass matrix. The superscript denotes the quantities of the unperturbed crystal. The eigenvalues of $\hat{D}^0$ are the squares of the normal mode frequencies $\omega_j^2(\underline{k})$ of the unperturbed lattice and they are specified by a wave vector $\underline{k}$ and branch index j. The eigenvalue equation is written as

$$\sum_{n,\beta} D'_{\alpha\beta}(\underline{m},\underline{n})\ \varphi_\beta\left(\frac{n}{\underline{k}j}\right) = \omega_j^2(kj)\ \varphi_\alpha\left(\frac{m}{\underline{k}j}\right). \tag{2.35}$$

The eigenvectors $\left\{\varphi\left(\frac{m}{\underline{k}j}\right)\right\}$ which are normalized plane waves travelling along x, y, z directions, satisfy the following orthonormality and closure relations.

$$\sum_{m,\alpha} \varphi_\alpha^*\left(\frac{m}{\underline{k}j}\right)\ \varphi_\alpha\left(\frac{m}{\underline{k}'j'}\right) = \delta_{\underline{k}\underline{k}'}\delta_{jj'}, \tag{2.36a}$$

$$\sum_{k,j} \varphi_\alpha^*\left(\frac{m}{\underline{k}j}\right)\ \varphi_\beta\left(\frac{n}{\underline{k}j}\right) = \delta_{\underline{m}\underline{n}}\ \delta_{\alpha\beta}. \tag{2.36b}$$

The explicit form for $\varphi_\alpha\left(\frac{m}{\underline{k}j}\right)$ is

$$\varphi_\alpha\left(\frac{m}{\underline{k}j}\right) = \frac{1}{\sqrt{N}}\ e^{i\underline{k}\cdot\underline{R}(\underline{m})}e_\alpha(\underline{k}j). \tag{2.37}$$

where $\left\{e(\underline{k}j)\right\}$ are the polarization vectors. Their orthonormality and closure properties follow from equations(2.36). For Bravais crystals $\underline{e}(\underline{k}j)$ are real. The normal mode frequencies satisfy the condition,

$$\omega_j(-\underline{k}) = \omega_j(\underline{k}). \tag{2.38}$$

The plane wave character of the lattice vibrations
is due to the translational invariance of the crystal. In
the presence of defects this is destroyed and the vibrations
depart from their plane wave nature. There are two distinct
ways of looking at the problem for its solution. The usual
method is to express the vibrations, the Green's functions
etc. in terms of the unperturbed one's whose properties are
well known. The alternative way is to look for a suitable
transformation which can diagonalize the perturbed dynamical
matrix. The eigenvalues of this matrix are the squares of the
normal mode frequencies of the perturbed crystal and hence[92]
cannot be labelled by the propagation vector $\underline{k}$ and branch
index j. In stead, they can be labelled by an index s which
runs from 1 to 3N. In practice such a transformation is
difficult to obtain explicitly. However, one can obtain a
formal solution of the problem which can be used later to
derive certain other useful relationships. The eigenvalue
equation of the perturbed lattice is

$$\sum_{r,\beta} D_{\alpha\beta} (\underline{m},\underline{n}) \; \varphi'_\beta \left( \frac{n}{s} \right) = \tilde{\omega}^2_s \; \varphi'_\alpha \left( \frac{m}{s} \right) \qquad (2.39)$$

where $\left\{ \tilde{\omega}^2_s \right\}$ are the new normal mode frequencies. The eigen-
vectors satisfy the following orthonormality and closure
relations.

$$\sum_{m,\alpha} \varphi'^*_\alpha \left( \frac{m}{s} \right) \; \varphi'_\alpha \left( \frac{m}{s'} \right) = \delta_{ss'}, \qquad (2.40a)$$

$$\sum_s \varphi'^*_\alpha \left( \frac{m}{s} \right) \; \varphi'_\beta \left( \frac{n}{s} \right) = \delta_{\underline{mn}} \, \delta_{\alpha\beta}. \qquad (2.40b)$$

It is convenient to use the first method for most of our calculations. The Fourier transform of equation (2.32) yields

$$\omega^2 \, \hat{F}(\omega) \;=\; \frac{\hat{D}}{2\pi} \;+\; \hat{F}(\omega) \, \hat{D} \, . \tag{2.41}$$

This is written in a more convenient manner as

$$F(\omega) \;=\; - \, \frac{1}{2\pi} \, [ \, \hat{I} - \omega^2 \, \hat{M}^{\frac{1}{2}} \, \hat{G} \, \hat{M}^{\frac{1}{2}} \, ] \tag{2.42}$$

where $\hat{I} =$ is the 3N dimensional unit matrix and

$$\hat{G} \;=\; (\hat{M}\omega^2 - \hat{A})^{-1} \, . \tag{2.43}$$

$\hat{G}$ is the Green's function matrix whose properties are discussed by Montroll and Potts. This Green's function was widely used to study the dynamical properties of pure crystals as well as crystals containing substitutional defects. Recently this technique has been applied to molecular lattices[104] and other impurity clusters which occur naturally as disorders involving a line or plane of defects.[105] The surface defects which gives an additional mode known as 'surface mode' has also been discussed in terms of this Green's function.[106] The unperturbed Green's function is given by

$$\hat{G}^{\,0} \;=\; (\hat{M}\omega^2 - \hat{A})^{0-1} \tag{2.44}$$

Any particular element of this Green's function is expressed as

$$G_{\alpha\beta}(\underline{m},\underline{n};\, \omega^2 \pm i\epsilon) = (M_{\underline{m}} M_{\underline{n}})^{-\frac{1}{2}} \sum_{kj} {}' \frac{\varphi_\alpha(\frac{m}{kj}) \, \varphi_\beta(\frac{n}{kj})}{\omega^2 - \omega_{kj}^2 \pm i\epsilon}$$

$$= \frac{1}{3N(M_{\underline{m}}M_{\underline{n}})^{\frac{1}{2}}} \sum_{\underline{k}j} \frac{e_\alpha(\underline{k}j)\, e_\beta(\underline{k}j)}{\omega^2 - \omega^2_{\underline{k}j} \pm i\varepsilon}\, e^{i\underline{k}\cdot(\underline{R}(\underline{m})-\underline{R}(\underline{n}))}.$$

$$(2.45)$$

The summation over $\underline{k}$ is over the first Brillouin zone.

Now one can obtain easily the velocity and displacement Green's functions in terms of $\hat{G}$ . Taking the Fourier transform of the equation(2.28) and equation(2.42) we have

$$\langle\!\langle \dot{\underline{U}}(o),\, \dot{\underline{U}}(t) \rangle\!\rangle_\omega = -\frac{1}{2\pi}\, [\hat{M}^{-1} - \omega^2\, \hat{G}] \qquad (2.46a)$$

Hence the displacement Green's function

$$\langle\!\langle \underline{U}(o),\, \underline{U}(t) \rangle\!\rangle = -\frac{1}{2\pi\cdot 2}\, [\hat{M}^{-1} - \omega^2\hat{G}] \qquad (2.46b)$$

The time correlation functions of the Green's functions are obtained with the help of equations(2.10) and equation(2.11).

$$\langle u_\beta(\underline{n},t)\, u_\alpha(\underline{m},o) \rangle = \text{Lim}_{\varepsilon \to 0} \frac{i}{2\pi}\int_{-\infty}^{+\infty} \frac{e^{i\omega t}\omega^2\, d\omega}{(e^{\beta\omega}-1)}.$$

$$[G_{\alpha\beta}(\underline{m},\underline{n};\omega^2 +i\varepsilon) - G_{\alpha\beta}(\underline{m},\underline{n};\omega^2 - i\varepsilon)] \qquad (2.47a)$$

$$\langle u_\beta(\underline{n},t)\, u_\alpha(\underline{m},o) \rangle = \text{Lim}_{\varepsilon \to 0} \frac{i}{2\pi}\int_{-\infty}^{+\infty} \frac{e^{i\omega t}\, d\omega}{(e^{\beta\omega}-1)}$$

$$[G_{\alpha\beta}(\underline{m},\underline{n};\omega^2 +i\varepsilon) - G_{\alpha\beta}(\underline{m},\underline{n};\omega^2 - i\varepsilon)] \qquad (2.47b)$$

It is clear from these expressions that in the harmonic approximation the Green's functions do not depend on temperature and hence any properties which are directly related to

Green's function become temperature independent. But the correlation functions do depend on temperatures. The general formula for correlation functions are valid for all times and for all temperatures. By making $\underline{m} = \underline{n}$, $\alpha = \beta$ and $t = 0$, the respective auto correlation functions are obtained and they express the mean square velocity and displacement of that particular atom. These two quantities are important in connection with Mössbauer effect where the resonant atom is generally a substitutional impurity in the crystal.

## § 2.5 Power Absorption

In presence of electromagnetic radiation the energy is continually transferred to the crystal due to interaction through the electric dipole moment. The strength of the absorption depends on the frequency of the exciting field and the nature of the phonon spectrum of the crystal. One of the convenient ways of studying the response of the system to the external radiation is to measure the power lost by the field. The expression for power absorption $B(\omega)$ per unit volume as a function of exciting frequency is obtained by taking the time average of the scalar product of the electric field with the current density i.e.

$$B(\omega)' = [\ \underline{E}(t) \cdot \langle \underline{J}(t) \rangle\ ]_{\text{Time Average}}$$

$$= [\ \sum_{\alpha} E_\alpha \cos\omega t \ \text{Re} \sum_{\beta} \sigma_{\alpha\beta}(\omega)\ E_\beta\ e^{i\omega t + \varepsilon t}]_{\text{Time Average}}$$

$$(2.48)$$

With the help of equations(2.29) and (2.42) it can be expressed in terms of the Green's function as

$$B(\omega) = \frac{1}{2} \sum_{\substack{m,n \\ \alpha,\beta}} e_{\underline{m}} \, e_{\underline{n}} \, E_{\alpha} \, E_{\beta} \quad \text{Im} \; G_{\alpha\beta}(\underline{m},\underline{n}; \omega^2 - i\varepsilon). \quad (2.49)$$

This is an exact expression[80] for the absorption line-shape function for a harmonic crystal when the absorption is due to one phonon process only. No specific model of the lattice is assumed in deriving this formula. The applicability of this formula depends on the evaluation of the Green's function and they are model dependent. In almost all the cases (except Debye model) the Green's functions are to be evaluated numerically with the help of high speed computors.

As has been pointed out earlier the harmonic Green's functions are independent of temperature, and hence the infrared absorption comes out to be temperature independent. However, in reality i.e. measurement of absorption co-efficient temperature comes into play a major role. A temperature factor can be incorporated in the theory if one considers higher order phonon processes arising out of the anharmonic terms in the potential energy or the non-linear terms in the electric moment or both together. But difficulties arise in solving the problem of defect together with anharmonicity or higher order dipole moment, as it yields a number of coupled equations involving higher order Green's functions.

The above expression which involves only one phonon

process can be obtained by solving classically the Newton's
equations for the displacements of the lattice. In the
presence of radiation, the charged impurities in otherwise
uncharged host or ions in polar crystals undergo forced
vibrations with the same frequency as that of the radiation,
but there is a phase shift[107] between the driving force and the
lattice vibrations. The expression for power absorption as a
function of the exciting frequency is obtained by taking the
time average of the scalar product of velocity of the charged
atom with the driving force and this depends on the phase
angle. Since the phase shift is related to the Green's func-
tion, the ultimate result comes out to be same as that of
equation(2.49).

## § 2.6 Sum Rule

Dawber and Elliott[71] have derived an expression for the
total integrated absorption over both the band and localized
modes. The contributions of both types of modes were calcu-
lated separately. For localized modes, they have assumed a
normalized shape function which takes into account the broad-
ening of the level due to anharmonic effects. However, one
can derive such a result for a general defect which involves
a change of force constant besides the change of mass in the
harmonic approximation without assuming any particular shape
for the localized mode.

The total absorption $B^T$ is defined as

$$B^T = \int\limits_{0}^{\infty} B(\omega)\,d\omega$$

$$= \frac{1}{2}\sum_{\substack{m,n \\ \alpha,\beta}} \int\limits_{0}^{\infty} e_{\underline{m}}\, e_{\underline{n}}\, E_{\alpha}\, E_{\beta}\, \omega\, \mathrm{Im}\, G_{\alpha\beta}(\underline{m},\underline{n};\omega^2 - i\varepsilon)\,d\omega \;.$$

$$(2.50)$$

As has been pointed out earlier that the perturbed dynamical matrix can be diagonalized by a unitary transformation, so that we can express the perturbed Green's function directly as

$$G_{\alpha\beta}(\underline{m},\underline{n},\omega^2 - i\varepsilon) = [\hat{M}^{-\frac{1}{2}}(\hat{I}\,\omega^2 - \hat{D})^{-1}\,\hat{M}^{-\frac{1}{2}}]_{\alpha\beta}^{\underline{m},\underline{n}}$$

$$= \frac{1}{(M_{\underline{m}}M_{\underline{n}})^{\frac{1}{2}}}\sum_{s} \frac{\varphi_{\alpha}(\frac{m}{s})\,\varphi_{\beta}^{*}(\frac{n}{s})}{\omega^2 - \omega^2_{s} - i\varepsilon} \qquad (2.51)$$

Hence

$$B^T = \frac{\pi}{2}\sum_{\substack{m,n \\ \alpha,\beta}} \frac{e_{\underline{m}} e_{\underline{n}}}{(M_{\underline{m}}M_{\underline{n}})^{\frac{1}{2}}}\, E_{\alpha} E_{\beta}\sum_{s} \varphi'_{\alpha}(\tfrac{m}{s})\,\varphi'^{*}_{\beta}(\tfrac{n}{s})\,\omega\,\delta(\omega^2 - \omega^2_{s})\,d\omega$$

$$(2.52)$$

Now the $\delta$-function integral is carried out easily. The closure relation given by(equation(2.40b) helps us to write

$$B^T = \frac{\pi}{4}\sum_{m,\alpha} \frac{e_{\underline{m}}^2 E_{\alpha}^2}{M_{\underline{m}}} \;.$$

$$(2.53)$$

This formula is quite general irrespective of any specific model of the crystal lattice, hence can be applied to the case of charged impurity as well as impurity in ionic crystals. No parameter characterising the interaction between the atoms occur in this expression. Only parameters which determines the total absorption, depends on the

impurity mass and its charge.

(i)   Charged Impurities:

For a dilute concentration of charged impurities ($N_I$ per unit volume) whose masses are $M'$ in otherwise uncharged host crystal, the total absorption is given by

$$B^T = \frac{\pi}{4} \frac{e^2 E^2 N_I}{M'}$$  (2.54)

(ii)   Impurities in Ionic Crystals:

We consider the ionic crystal as consisting of two types of masses ($M_1$ and $M_2$) with charges $-e$ and $+e$ at odd and even sites respectively. If $N_I$ impurities with charge $+e$ and mass $M'_1$ are substituted at the odd sites the total absorption comes  out to be

$$B^T = \frac{\pi e^2 E^2}{8} [(\frac{1}{M_1} + \frac{1}{M_2}) + 2\frac{N_I}{N}(\frac{1}{M_1'} - \frac{1}{M_1})]$$

(2.55)

It has been pointed out by Angress[66] et al. that the effective charge of an impurity can be estimated from the total area of the absorption curve provided the concentration of the impurities is known. Maradudin[98] has also obtained a similar expression for the total absorption.

CHAPTER III

ABSORPTION LINE SHAPE DUE TO CHARGED IMPURITIES

## § 3.1  Lattice Model And Perturbation

For a perfect harmonic lattice the amplitude of
vibrations are plane waves.  It is well known that in the
presence of defect due to the loss of translational symmetry,
the vibrations depart from their plane wave characters.
Since the perturbation is local one, the modes are strongly
perturbed near the vicinity of the defect, and hence these
modes can be studied best by using as a probe some property
of the defect itself.  In case of crystals which do not
possess a first order electric moment the introduction of an
impurity with non zero effective charge leads to absorption
of photon by creation of one phonon over the entire range
of lattice modes.

A charged substitutional impurity in a crystal
excited by monochromatic radiation is one of the simplest
example of a forced oscillator coupled to a large system.
An oscillator coupled to a system with many degrees of free-
dom and continuous spectrum behaves like a damped oscillator,
the damping being due to the continual transfer of energy
from the oscillator to other modes of the system.  The absor-
ption line shape of a charged substitutional impurity would

therefore, be intimately related to the structure of the frequency spectrum of the crystal with the impurity. In reality the optical absorption occurs through one and multi phonon processes, but the one phonon process is of primary importance, the multi phonon process leading to a background against which the one phonon absorption is thrown into relief. It is known that absorption spectra of type I diamond arises due to nitrogen impurities.[108]

Recently there have been considerable interests in the field of phonon scattering by defects, specifically due to the presence of quasi-localised mode in the acoustic band which mani-fests in resonant scattering. Callaway,[28,109] Takeno,[24] Wagner,[38] Krumhansl,[110,111] Thoma and Ludwig[112] and Gunther[79] have considered the details of the problem with particular interest in the resonant scattering. Krumhansl and Mathew considered the problem of one dimensional lattice in a rather complete way. Elliott and Taylor[103] used the double time thermodynamic Green's function to solve the isotope defect. Visscher[90] has discussed a different aspect of the defect vibration which is of importance in the Mossbauer effect. Yussouff and Mahanty[113,114] and Klein[115,116] have given general theories of scattering of phonons in cubic crystals. Group theoretic method was applied by Callaway,[109] to separate out the scattering amplitude into its various symmetry parts characterised by different irreducible

representations of the point group of the lattice and it
was followed up by the other workers. All these studies
lead in a natural way to the exact evaluation of the Green's
functions of the perturbed lattice when the impurity atom
involves both a change of mass as well as the nearest neigh-
bours force constant.

We consider here the case of one defect in the
crystal and its effect on the vibrational properties. In
reality the crystal contains a number of impurities, but
in many physical situations where the impurity concentra-
tion is very low one obtains a good approximation for many
impurities in the crystal by multiplying the effect produced
by a single impurity by the total number of impurities.
This is the case for example in impurity induced infrared
absorption in ionic and homopolar crystals where the impur-
ity concentration rarely exceed $10^{18}$ per $cm^3$: In this
process one neglects the impurity-impurity interaction which
gives rise to effects in higher order of concentration.

Knowledge of perturbed Green's function is indis-
pensable in calculating various properties of impure crystals.
This depends on the structure of the crystal as well as the
interacting forces among its constituent atoms. One cannot
proceed to calculate the detailed behaviour of a crystal
without considering any specific model. Any realistic model
becomes almost intractable due to heavy numerical computations

which sometimes obscure the physical situation to a considerable extent.

We consider monatomic cubic lattices (simple cubic, body-centered cubic and face-centered cubic) and investigate the cases where the polarization does not enter into the picture. The lattice consists of N atoms each of them having mass M. The harmonic interactions are limited upto the nearest neighbours in such a way that the three cartesian components of the displacement vector become independent of each other. In this so called scalar model the phonons are not polarized. Such unrealistic lattice models are chosen for mathematical simplicity in analysis, however many of the features of optical absorption by impurity in this model are of sufficient generality to be applicable to more realistic models. For the study of low frequency impurity modes which are being discussed here, such a simple but mathematically tractable model is particularly useful because the low frequency behaviour of phonons is not so sensitive to the crystal model.

The lattice sites are denoted by a vector $\underline{R}$ given by

$$\underline{R}_S = la\,\hat{e}_1 + ma\,\hat{e}_2 + na\,\hat{e}_3 \, , \qquad (3.1a)$$

$$\underline{R}_B = (l + \frac{m}{2})a\,\hat{e}_1 + \frac{m}{2}a\,\hat{e}_2 + (n + \frac{m}{2})a\,\hat{e}_3 \, , \qquad (3.1b)$$

$$\underline{R}_F = \frac{1}{2}(l+n)a\,\hat{e}_1 + \frac{1}{2}(l+m)a\,\hat{e}_2 + \frac{1}{2}(m+n)a\,\hat{e}_3 \, . \qquad (3.1c)$$

Here a is the lattice constant and (l,m,n) are any integers
(zero included). $(\hat{e}_1, \hat{e}_2, \hat{e}_3)$ are unit vectors along x,y and
z directions respectively. The subscript S,B and F denote
respectively the simple cubic, body-centered cubic and face-
centered cubic lattices. The time independent equations of
motion of the lattice in the matrix form is

$$(\hat{M}\omega^2 - \hat{A})\ \underline{U} = 0. \tag{3.2}$$

where the force constant matrix A has the following structure

$$A_S(l,m,n/l',m',n') = \gamma[6\ \delta_{ll'}\ \delta_{mm'}\ \delta_{nn'} - \delta_{mm'}\ \delta_{nn'}$$

$$(\delta_{l+1,l'} + \delta_{l-1,l'})$$

$$- \delta_{ll'}\ \delta_{nn'}\ (\delta_{m+1,m'} + \delta_{m-1,m'})$$

$$- \delta_{ll'}\ \delta_{mm'}\ (\delta_{n+1,n'} + \delta_{n-1,n'})], \tag{3.3a}$$

$$A_B(l,m,n/l',m,n') = \gamma[3\ \delta_{ll'}\ \delta_{mm'}\ \delta_{nn'} - \delta_{ll'}\ \delta_{nn'}$$

$$(\delta_{m,m+1} + \delta_{m',m-1})$$

$$- \delta_{nn'}(\delta_{l,l+1}\ \delta_{m',m-1} + \delta_{l',l-1}\ \delta_{m',m+1})$$

$$- \delta_{ll'}(\delta_{m',m-1}\ \delta_{n',n+1} + \delta_{m',m+1}\ \delta_{n',n-1})$$

$$- (\delta_{l',l+1}\ \delta_{m',m-1}\ \delta_{n',n+1} + \delta_{l',l-1}\ \delta_{m',m+1}$$

$$\delta_{n',n-1})]\ , \tag{3.3b}$$

and

$$A_F(l,m,n/l',m',n') = \gamma[12\delta_{ll'}\,\delta_{mm'}\,\delta_{nn'} - \delta_{ll'}\delta_{mm'}(\delta_{n',n+1} + \delta_{n',n-1})$$

$$- \delta_{ll'}\,\delta_{nn'}(\delta_{m',m+1} + \delta_{m',m-1}) - \delta_{mm'}\,\delta_{nn'}(\delta_{l',l+1} + \delta_{l',l-1})$$

$$- \delta_{ll'}(\delta_{m',m+1}\,\delta_{n',n-1} + \delta_{m',m-1}\,\delta_{n',n+1})$$

$$- \delta_{mm'}(\delta_{l',l+1}\,\delta_{n',n-1} + \delta_{l',l-1}\,\delta_{n',n+1})$$

$$- \delta_{nn'}(\delta_{l',l+1}\,\delta_{m',m-1} + \delta_{l',l-1}\,\delta_{m',m+1})]. \tag{3.3c}$$

The solutions of equation (3.2) are the plane waves given by

$$U(\underline{R}) = \frac{1}{\sqrt{N}}\,e^{i\underline{k}\cdot\underline{R}/a} \quad . \tag{3.4}$$

Substituting equation(3.4) in equation(3.2) and making use of the equations(3.3) the frequency of wave-vector relations are obtained as

$$\omega_S^2\,(\underline{k}) = \frac{2\gamma}{M}\,[\,3 - \cos k_1 - \cos k_2 - \cos k_3] \quad ,\tag{3.5a}$$

$$\omega_B^2\,(\underline{k}) = \frac{8\gamma}{M}\,[\,1 - \cos\tfrac{1}{2}k_1\cdot\cos\tfrac{1}{2}k_2\cdot\cos\tfrac{1}{2}k_3] \quad , \tag{3.5b}$$

$$\omega_F^2\,(\underline{k}) = \frac{4\gamma}{M}\,[\,3 - \cos\tfrac{1}{2}k_1\cdot\cos\tfrac{1}{2}k_2 - \cos\tfrac{1}{2}k_2\cdot\cos\tfrac{1}{2}k_3$$

$$- \cos\tfrac{1}{2}k_3\cdot\cos\tfrac{1}{2}k_1] \quad . \tag{3.5c}$$

It is convenient to assume that the substitutional impurity whose mass is $M+\triangle M$ is substituted at the origin. The nearest neighbours are coupled to it by force constant

$\gamma + \triangle \gamma$. So the perturbation is limited to the impurity site and its nearest neighbours. The model of a simple cubic lattice with impurity is shown in Fig. 1. In presence of this perturbation the equation of motion becomes

$$(M\omega^2 - \hat{A}) \underline{U} = [(\hat{M}\omega^2 - \hat{A})^0 + \hat{P}] \underline{U} = 0. \qquad (3.6)$$

The elements of the $\hat{P}$ matrix are given by

$$P(\underline{0},\underline{0}) = M\omega^2 - n\triangle\gamma \quad,$$

$$P(\underline{R_n} , \underline{R_n}) = -\triangle\gamma \quad,$$

$$P(\underline{0},\underline{R_n}) = P(\underline{R_n},\underline{0}) = \triangle\gamma \quad. \qquad (3.7)$$

where n is the number of nearest neighbours. It has value 6 for simple cubic, 8 for body-centered cubic, and 12 for face-centered cubic respectively.

The equation relating the perturbed and unperturbed Green's function follows from equations (2.43) and (3.6) as

$$\hat{G} = \hat{G}^0 - \hat{G}^0\hat{P}\hat{G} . \qquad (3.8)$$

For many impurities the perturbation matrix $\hat{P}$ has several blocks and the equation (3.8) is the Dyson's equation. For many impurities the exact solution is difficult and one solves the problem by iteration. The formal solution of the above equation is

$$\hat{G} = (\hat{I} + \hat{G}^0\hat{P})^{-1}\hat{G}^0 ; \qquad (3.9)$$

SIMPLE CUBIC LATTICE MODEL WITH IMPURITY

$\odot$ = M

$\bullet$ = M + $\Delta$M

— = $\gamma$

$\sim\!\!\sim\!\!\sim$ = $\gamma + \Delta\gamma$

(0,1,0)

(0,0,1)

(-1,0,0)     (0,0,0)     (1,0,0)

(0,0-1)

(0,-1,0)

FIG. I
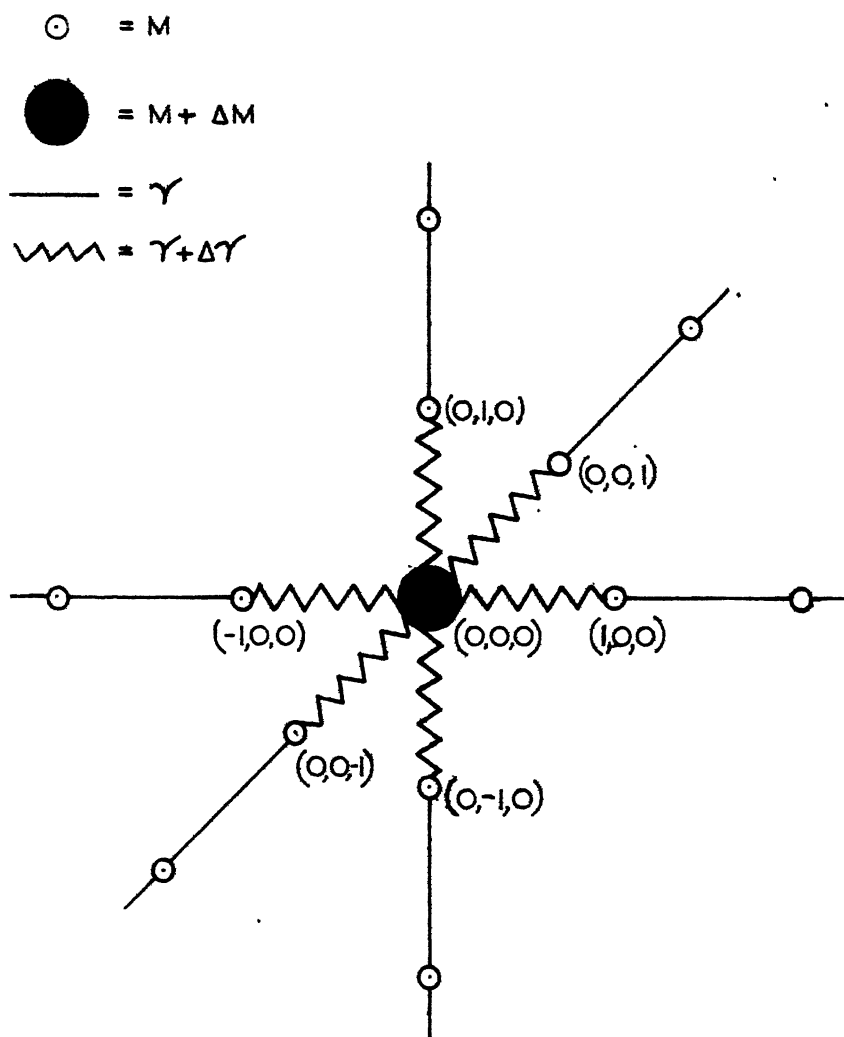
For one impurity the perturbation matrix has only a small
number of non-vanishing elements constituting a submatrix
the dimensionality of which is determined by the extent of
the perturbation. This helps us to write $\hat{P}$ matrix in the
following partitioned form

$$\hat{P} = \begin{pmatrix} \hat{p} & \hat{0} & \hat{0} & \cdots \\ \hat{0} & \hat{0} & \hat{0} & \cdots \\ \hat{0} & \hat{0} & \hat{0} & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix} \qquad (3.10)$$

where $\hat{p}$ is the non-vanishing block in the perturbation matrix.
Its dimensionality is 7,9,13 for simple cubic, body-centered
cubic, and face-centered cubic lattices respectively. The
unperturbed Green's function matrix can be partitioned in a
similar manner i.e.

$$G^O = \begin{pmatrix} \hat{g} & \hat{g}_{12} & \hat{g}_{13} & \cdots \\ \hat{g}_{21} & \hat{g}_{22} & \hat{g}_{23} & \cdots \\ \hat{g}_{31} & \hat{g}_{32} & \hat{g}_{33} & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix} \qquad (3.11)$$

where each of the sub-matrices of $\hat{G}^O$ has the same dimen-
sionality as that of $\hat{p}$. With the help of these two equations
$(\hat{I} + \hat{G}^O\hat{P})$ takes the form as

$$\hat{I}+\hat{G}\hat{P} = \begin{pmatrix} \hat{I} + \hat{g}p & \hat{0} & \hat{0} & \cdots \\ \hat{g}_{21}\,\hat{p} & \hat{I} & \hat{c} & \cdots \\ \hat{g}_{31}\,\hat{p} & \hat{0} & I & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix} \qquad (3.12)$$

The inverse of this matrix is easy to work out, because
it involves the inverse matrix of $(\hat{I} + \hat{g}\hat{p})$ whose dimension-
ality is small. Hence the perturbed Green's function
becomes

$$\hat{G} = \begin{pmatrix} (\hat{I}+\hat{g}\hat{p})^{-1} & \hat{0} & \hat{0} & \cdots \\ -\hat{g}_{21}\hat{p}(\hat{I}+\hat{g}\hat{p})^{-1} & \hat{I} & \hat{0} & \cdots \\ -\hat{g}_{31}\hat{p}(\hat{I}+\hat{g}\hat{p})^{-1} & \hat{0} & \hat{I} & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix} \begin{pmatrix} \hat{g} & \hat{g}_{12} & \hat{g}_{13} & \cdot\cdot \\ \hat{g}_{21} & \hat{g}_{22} & \hat{g}_{23} & \cdot\cdot \\ \hat{g}_{31} & \hat{g}_{32} & \hat{g}_{33} & \cdot\cdot \\ \cdot & \cdot & \cdot & \cdot\cdot \end{pmatrix}$$

$$(3.13)$$

This is the general form of the perturbed Green's
function matrix. Any element of it which is required for
the specific calculation can be obtained by considering the
appropriate block of this matrix. In fact, as far as the
optical absorption due to charged impurities is concerned
one needs some definite element which makes it simpler to
select the block.

## 3.2 Absorption Line Shape

Since the impurity having charge 'e' at the origin

we have

$$e_i = e \, \delta_{i,0} \quad .$$  (3.14)

Then the absorption line shape formula given by equation(2.49) reduces to

$$B(\omega) = \tfrac{1}{2} \, e^2 \, E^2 \omega \, \text{Im} \quad G \, (0,0, \omega^2 - i\varepsilon)$$  (3.15)

It is clear now that only the $(0,0)$ element of the perturbed Green's function enters into the calculation. This can be obtained from the 1st block of the matrix given by equation (3.13).

$$G(0,0,\omega^2 - i\varepsilon) = [(\hat{I} + \hat{g}\hat{p})^{-1}\hat{g}]_{0,0} \quad .$$  (3.16)

This element can be calculated by using the explicit form of $\hat{p}$ and $\hat{g}$ matrices and then inverting the matrix $(\hat{I} + \hat{g}\hat{p})$ directly. However, this inversion can be achieved in a more elegant way by taking into account the symmetry of the system. This method not only saves the labour, but throws some more light on the nature of the vibrations of the impurity which would have been otherwise obscure in the direct calculations.

Although the defect destroys the translational symmetry, the point group symmetry of the crystal about the impurity site as the reference point is still retained. This enables one to use the displacements of all the affected sites

in forming a reducible representation $\Gamma$ of the point group of the lattice, which can be decomposed in terms of irreducible representations $\Gamma^{(\nu)}$ of the point group as

$$\Gamma = \sum_{\nu}^{i} a_{\nu} \Gamma^{(\nu)} \quad . \tag{3.17}$$

where $a_{\nu}$ are zero or integers. The matrices $\hat{p}$ and $\hat{g}$ have the symmetry of the point group of the lattice and hence, one can find out a unitary matrix $\hat{V}$ which block diagonalizes $\hat{p}$, $\hat{g}$, and any function of them, namely $(\hat{I}+\hat{g}\hat{p})$. Such a matrix can be found by group theoretic procedure. The number of such blocks, the dimensionality[117] of each block etc.. are known from the equation(3.17). If $\Gamma^{(\nu)}$ has the dimensionality $n_{\nu}$ , then in block diagonal form there will be $n_{\nu}$ identical $a_{\nu}$ x $a_{\nu}$ blocks. The cubic crystals whose point group symmetry is $O_h$ the reducible representation $\Gamma$ is decomposed into its various irreducible representations in the usual notation[118] as

$$\Gamma_S = 2 A_{1g} + F_{1u} + E_g \quad , \tag{3.18a}$$

$$\Gamma_B = 2 A_{1g} + F_{1u} + F_{2g} + A_{2u} , \tag{3.18b}$$

$$\Gamma_F = 2 A_{1g} + F_{1u} + E_g + F_{2g} + F_{2u} \quad . \tag{3.18c}$$

This shows the various symmetry vibrations possible in the cubic lattices. The $\hat{V}$ matrix is constructed with the help of projection operator and is given in the appendix I. The rows and columns of the $\hat{p}$, $\hat{g}$, and $\hat{V}$ matrices are labelled

in same manner. For example in case of simple cubic lattice the rows and columns are labelled as (000), (100), (010), (001), (-100), (0-10) (00-1).

The block diagonal form of $(\hat{I}+\hat{g}\hat{p})^{-1}$ for simple cubic lattice is given by

$$
\hat{T}^{-1} = \begin{pmatrix} \hat{T}_1^{-1} & 0 & 0 & 0 & 0 & 0 \\ 0 & T_2^{-1} & 0 & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & T_6^{-1} \end{pmatrix} \qquad (3.19)
$$

where the various blocks are as follows. $\hat{T}_1^{-1}$ is a two dimensional matrix belonging to s-wave ($A_{1g}$) part. Its explicit form is

$$
\hat{T}_1^{-1} = \frac{1}{D_S^s} \begin{pmatrix} 1 + \triangle M \omega^2 \frac{\triangle \gamma}{\gamma} g_1 & -\sqrt{6}\,\triangle\gamma(g_{os}-g_1) \\ -\sqrt{6} M\omega^2 g_1(\frac{\triangle M}{M} - \frac{\triangle\gamma}{\gamma}) & 1+ \frac{\triangle\gamma}{\gamma} +(1- \frac{\triangle\gamma}{\gamma})\, M\omega^2 g_{os} \end{pmatrix}
$$

$$(3.20a)$$

and

$$
T_2^{-1} = T_3^{-1} = T_4^{-1} = \frac{1}{D_S^p} \; , \quad (F_{1u}) \text{ p- wave parts.} \quad (3.20b)
$$

$$
T_5^{-1} = T_6^{-1} = \frac{1}{D_S^d} \; , \quad (E_g) \text{ d- wave parts.} \qquad (3.20c)
$$

where $\text{Det}(\hat{I}+\hat{g}\hat{p}) = |\hat{I} + \hat{g}\hat{p}| = D_S^s (D_S^p)^3 (D_S^d)^2.$ $\qquad (3.20d)$

The nomenclature s, p, d (used here as superscripts) corresponding to the irreducible representations $A_{1g}$, $F_{1u}$, and $E_g$ are used to describe the partial wave amplitudes of vibration. They have acquired such names in analogy with the symmetry of s, p, d wave functions in a cubic crystal. The explicit forms of the factors of the determinant are

$$D_S^s = 1 + \frac{\Delta\gamma}{\gamma} + \frac{M\omega^2}{6\gamma}\frac{\Delta\gamma}{\gamma}\left(1+\frac{\Delta M}{M}\right) - M\omega^2\left[-\frac{\Delta M}{M}\left(1+\frac{\Delta\gamma}{\gamma}\right) + \right.$$

$$\left. \frac{M\omega^2}{6\gamma}\frac{\Delta\gamma}{\gamma}\left(1+\frac{\Delta M}{M}\right)\right]g_{os} \quad , \quad (3.21a)$$

$$D_S^p = 1 - \Delta\gamma\,(g_{os} - g_{11}) \quad , \quad (3.21b)$$

$$D_S^d = 1 - \Delta\gamma\,(g_{os} + g_2 - 2g_{11}). \quad (3.21c)$$

The four different elements of the Green's function used above are given below.

$$g_{os} = G^0(000,\ 000;\ \omega^2 - i\varepsilon) \quad (3.22a)$$

$$g_1 = G^0(000,\ \pm 100;\ \omega^2 - i\varepsilon) \quad (3.22b)$$

(Any permutations of the indices)

$$g_{11} = G^0(\pm 100,\ 0 \pm 10;\ \omega^2 - i\varepsilon) \quad (3.22c)$$

$$g_2 = G^0(\pm 100,\ \mp 100;\ \omega^2 - i\varepsilon) \quad (3.22d)$$

Evaluation of these Green's functions are possible by numerical methods which are well known.

In the above calculation $T_1^{-1}$ contains all the four different elements of the Green's functions, but the existence of some identity relations among these elements simplifies this to its present form. These relations can be deduced from the definition of the Green's function matrix for the perfect lattice i.e.

$$(\hat{M}\omega^2 - \hat{A})\; \hat{G}^0 = \hat{I} \; . \tag{3.23}$$

Or taking $(\underline{j},\underline{j}')$ element on both sides, we have

$$\sum_{\underline{n}} (\hat{M}\omega^2 - \hat{A})_{\underline{j},\underline{n}}\; \hat{G}^0_{\underline{n},\underline{j}} = \delta_{\underline{j},\underline{j}} \tag{3.24}$$

Now by making use of the equation(3.3a) and equations(3.22) the following relations are obtained

$$(M\omega^2 - 6\gamma)\; g_{os} + 6\gamma\; g_1 = 1 \quad , \tag{3.25a}$$

$$(M\omega^2 - 6\gamma)\; g_1 + \gamma\; (g_{os} + 4g_{11} + g_2) = 0 \; . \tag{3.25b}$$

From equations(3.20) it is clear that only the s-wave part of the determinant involves both the parameters $(\frac{\Delta M}{M}, \frac{\Delta \gamma}{\gamma})$ of the perturbation. The p and d parts depend only on the change of force constant. In case of isotopic impurity only this mode of vibration is possible. With this decomposition of the perturbed Green's function, its $(\underline{0},\underline{0})$ element is obtained as

$$G_S(\underline{0},\underline{0}; \omega^2 - i\varepsilon) = [\hat{V}_S \; \hat{T}^{-1} \hat{V}_S \hat{g}]_{\underline{0},\underline{0}}$$

$$= \frac{\left\{1 + \frac{\Delta\gamma}{\gamma}(1 - \frac{M\omega^2}{6\gamma})\right\} g_{0s} + \frac{1}{6\gamma} \frac{\Delta\gamma}{\gamma}}{D_S^s} \; , \quad (3.26)$$

The interesting point to be mentioned here is that, the $(\underline{0},\underline{0})$ element contains only the s-wave block corresponding to the totally symmetric one dimensional irreducible representation of the point group of the lattice, hence this mode becomes infrared active. This statement is valid not only for cubic lattices, but for all lattices which are monatomic and have the symmetry of any one of the point groups.[107] This is proved in appendix I. The pysical reasoning lies in the fact that except the s-eave mode the impurity does not take part in other modes of vibration although its nearest neighbours do move. This is because the p-like (three fold degenerate) and d-like (two fold degenerate) modes have nodes at the impurity site. Since the impurity atom is charged the dipole moment contribution comes only from the s-wave mode.

Since the columns of the $\hat{V}$ matrix are normalized vectors which are obtained from a general vector characterizing the displacements of the affected sites by projection operator, they represent the specific symmetry mode vibrations of the affected sites. The various symmetry modes belonging to the different irreducible representations given

by equation(3.18a) are shown schematically in Fig. 2.

Since the other two modes are not infrared active they cannot be studied by optical absorption experiments. In this respect the impurity and its nearest neighbour vibrations resemble a molecular vibration problem. The $(\underline{0},0)$ elements of the perturbed Green's functions for bcc and fcc lattices can be obtained in a similar manner. All these above discussions and arguments hold in those cases and we write them as

$$G_B(\underline{0},\underline{0};\omega^2-i\varepsilon) = \frac{\left\{1+(1-\frac{M}{8\gamma}\omega^2)\frac{\Delta\gamma}{\gamma}\right\}g_{0B}+\frac{1}{8\gamma}\frac{\Delta\gamma}{\gamma}}{D_B^S}, \quad (3.27a)$$

$$G_F(\underline{0},\underline{0};\omega^2-i\varepsilon) = \frac{\left\{1+(1-\frac{M}{12\gamma}\omega^2)\frac{\Delta\gamma}{\gamma}\right\}g_{0F}+\frac{1}{12\gamma}\frac{\Delta\gamma}{\gamma}}{D_F^S}. $$
$$(3.27b)$$

where

$$D_B^S = 1+\frac{\Delta\gamma}{\gamma} + \frac{\Delta\gamma}{\gamma}(1+\frac{\Delta M}{M})\frac{M\omega^2}{8\gamma} - M\omega^2[\frac{\Delta\gamma}{\gamma}(1+\frac{\Delta M}{M})\frac{M\omega^2}{8\gamma}$$

$$- \frac{\Delta M}{M}(1+\frac{\Delta\gamma}{\gamma})]g_{0B}, \quad (3.28a)$$

$$D_F^S = 1+\frac{\Delta\gamma}{\gamma} + \frac{\Delta\gamma}{\gamma}(1+\frac{\Delta M}{M})\frac{M\omega^2}{12\gamma} - M\omega^2[\frac{\Delta\gamma}{\gamma}(1+\frac{\Delta M}{M})\frac{M\omega^2}{12\gamma}$$

$$- \frac{\Delta M}{M}(1+\frac{\Delta\gamma}{\gamma})]g_{0F}. \quad (3.28b)$$

The present forms of equations(3.28) are obtained by using the following relationships among the elements of the Green's function and they are similar to equations(3.25)

SYMMETRY MODES IN SIMPLE CUBIC LATTICE
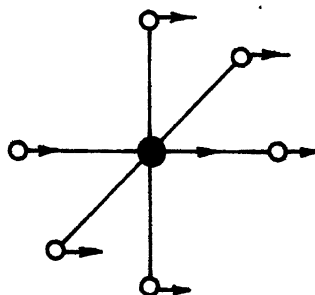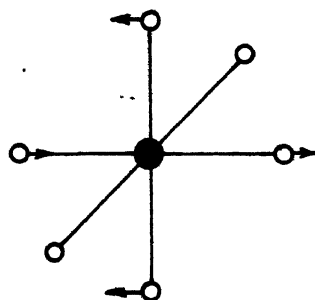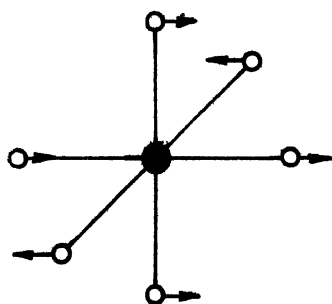
(a)  S - TYPE - MODE

(b)  d - TYPE MODE
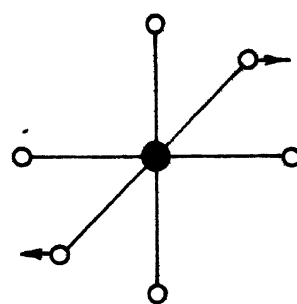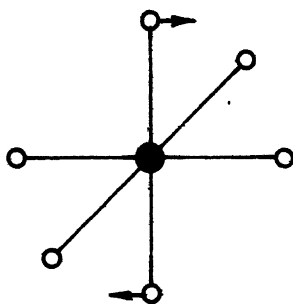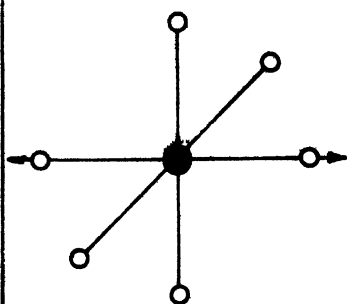
(C)-  p-TYPE MODE

FIG. 2

For bcc, $(M\omega^2 - 8\gamma)g_{0B} + 8\gamma\, g_{1B} = 1,$         (3.29a)

$$(M\omega^2 - 8\gamma)g_{1B} + \gamma\,(g_{0B} + 3g_{2B} + 3g_{3B} + g_{4B}) = 0 \;.$$

                                                                 (3.29b)

where

$$g_{0B} = G_B^O\,(0,0,0,\,\underline{0};\omega^2 - i\varepsilon) \;, \tag{3.30a}$$

$$g_{1B} = G_B^O\,(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2},\underline{0};\omega^2 - i\varepsilon) \;, \tag{3.30b}$$

$$g_{2B} = G_B^O\,(1,0,0,\underline{0};\omega^2 - i\varepsilon) \;, \tag{3.30c}$$

$$g_{3B} = G_B^O\,(1,1,0,\underline{0},\omega^2 - i\varepsilon) \;, \tag{3.30d}$$

$$g_{4B} = G_B^O\,(1,1,1,\underline{0},\omega^2 - i\varepsilon) \;. \tag{3.30e}$$

For fcc,

$$(M\omega^2 - 12\gamma)g_{0F} + 12\gamma\, g_{1F} = 1 \;, \tag{3.31a}$$

$$(M\omega^2 - 12\gamma)g_{1F} + \gamma(g_{0F} + 4g_{1F} + 2g_{2F} + 4g_{3F} + g_{4F}) = 0. \tag{3.31b}$$

where

$$g_{0F} = G_F^O\,(0,0,0,\underline{0},\omega^2 - i\varepsilon) \;, \tag{3.32a}$$

$$g_{1F} = G_F^O\,(\tfrac{1}{2},\tfrac{1}{2},0,\underline{0};\omega^2 - i\varepsilon) \;, \tag{3.32b}$$

$$g_{2F} = G_F^O\,(1,0,0,\underline{0};\omega^2 - i\varepsilon) \;, \tag{3.32c}$$

$$g_{3F} = G_F^O\,(1,\tfrac{1}{2},\tfrac{1}{2},\underline{0},\omega^2 - i\varepsilon) \;, \tag{3.32d}$$

$$g_{4F} = G_F^O\,(1,1,0,\underline{0},\omega^2 - i\varepsilon) \;. \tag{3.32e}$$

The ($\underline{C}$,$\underline{C}$) elements in all these three cases are similar except the structure factor and their Green's functions. Hence one can write a single expression for the line shape function for power absorption as

$$B(\omega) = \tfrac{1}{2}\, e^2 E^2 (1 + \tfrac{\Delta\gamma}{\gamma})^2 \;\; \frac{\omega \;\; \text{Im } g_0}{[\text{Re}D^S]^2 + [\text{Im}D^S]^2} \; . \quad (3.33)$$

where Re $D^S$ and Im$D^S$ denote the real and imaginary parts respectively of the resonant denominator $D^S$. Taking the computed values of $g_0$ for various frequencies the power absorption can be plotted for the three different crystals.

### 3.3 Discussion

The poles of the perturbed Green's function determines the new features in the spectrum of the lattice. Considering the equation (3.9) we obtain the equation

$$\text{Det} \quad (\hat{I} + \hat{G}^0 \hat{P}) = |\hat{I} + \hat{g}\, \hat{p}| = 0 \cdot \quad (3.34)$$

which gives all the characteristic frequencies of the impurity modes. This determinant is a product of several factors as discussed earlier. All of them are wholly real outside the band and the roots (if any) lying in that region are the localized mode frequencies. Since there is no imaginary parts, the life time of those modes are infinite. These local modes belong to different symmetry as they are obtained from different partial wave parts of the determinant.

Inside the band these equations are complex, the real parts of which may vanish depending on the strength of the perturbation. If the imaginary part is small at a frequency for which the real part vanishes, a resonant mode is created. One can calculate the life time of such a mode in the following way.

The density of states for the squared frequencies is given by

$$\rho(\omega^2) = \frac{1}{3N} \sum_s \delta(\omega^2 - \omega_s^2) = \frac{Im}{3N\pi} \sum_s' \frac{1}{\omega^2 - \omega_s^2 - i\varepsilon}$$

(3.35)

Using the orthogonality relation (2.40) this reduces to

$$\rho(\omega^2) = \frac{Im}{3N\pi} Tr(\hat{M}^{\frac{1}{2}} \hat{G} \hat{M}^{\frac{1}{2}}) ,$$

$$= \frac{Im}{3N\pi} [M Tr\hat{G}^0 + \Delta MG(\underline{0},\underline{0}) - M Tr \hat{G}^0\hat{P}(\hat{I}+\hat{G}^0\hat{P})^{-1}\hat{G}^0].$$ (3.36)

With some manipulations the expression becomes

$$\rho(\omega^2) + \Delta\rho(\omega^2) = \frac{Im}{3N\pi} [M Tr\hat{G}^0 + \frac{d}{d\omega^2} \log|\hat{I}+\hat{G}^0\hat{P}|] .$$ (3.37)

where

$$\rho_c(\omega^2) = \frac{Im}{3N\pi} M Tr G^0 = \frac{M}{\pi} Im g_0(\omega^2 - i\varepsilon) .$$ (3.38)

= density of states for squared frequencies
  for unperturbed lattice.

The change in squared density of states is

$$\Delta P(\omega^2) = \frac{\text{Im}}{N\pi} \frac{d}{d\omega^2} \log \left| \hat{I} + \hat{g}\hat{p} \right|$$

$$= \frac{\text{Im}}{N\pi} \sum_i \frac{D'^i}{D^i} . \qquad (3.38b)$$

where i takes all the factors of the determinant. These additional terms superimpose on the unperturbed density of states. The piculiarities arises due to the denominators $D^i$. Suppose there is a resonance in the i-th channel, then the change in the density of states in this mode is

$$\Delta P_i(\omega^2) = \frac{1}{N\pi} \text{Im} \frac{D'^i}{D^i} = \frac{1}{N\pi} \frac{\text{Re}D^i \text{Im}D'^i - \text{Re}D'^i \text{Im}D^i}{[\text{Re}D^i]^2 + [\text{Im}D^i]^2} . \quad (3.39)$$

If $\omega_i$ is the resonant mode frequency i.e. $\text{Re}D^i(\omega_i^2) = 0$, then we can expand $\text{Re}D^i$ in the neighbourhood of $\omega_i^2$ as

$$\text{Re}D^i = \text{Re}D'^i(\omega_i^2)(\omega^2 - \omega_i^2) + \dots \qquad (3.40)$$

The higher order terms are neglected. So the approximate form of equation (3.39) in the neighbourhood of $\omega_i$ reduces to a Lorentzian shape.

$$\Delta P_i(\omega^2) = \frac{1}{\pi N} \frac{\Gamma_i(\omega^2)}{(\omega^2 - \omega_i^2)^2 + \Gamma_i(\omega^2)} . \qquad (3.41a)$$

with a width given by

$$\Gamma_i(\omega^2) = - \frac{\text{Im}D^i(\omega^2)}{[\text{Re}D'^i(\omega^2)]_{\omega_i}} . \qquad (3.41b)$$

Knowing the resonance frequency one can calculate the width of the resonant level.

In view of the above discussion the absorption line shape function can be expressed in terms of the frequency distribution function as

$$B(\omega) = \frac{\pi e^2 E^2}{4M} \frac{\mathcal{F}(\omega)}{[\text{Re}D^S]^2 + [\text{Im}D^S]^2} \; . \qquad (3.42)$$

where

$$\mathcal{F}(\omega) = 2\omega \mathcal{F}(\omega^2)$$

$$= \text{frequency distribution function of the}$$
$$\text{unperturbed lattice.}$$

The denominator $D^S$ gives the additional structure to the phonon density of states. In case of an usual atom ( $\frac{\Delta M}{M} = 0$, $\frac{\Delta \gamma}{\gamma} = 0.$) being ionized the absorption spectrum directly reveals the frequency distribution function. This enables one to determine the one phonon density of states for the host crystal if the impurity is really isotopic and $\frac{\Delta M}{M} \simeq 0$. But the line shape function undergoes drastic modifications when the impurity is accompanied by a change of mass or force constant.

The absorption line shape due to an isotopic impurity in simple cubic lattice is illustrated in Fig. 3. The unperturbed density of states is shown by the curve Fig. 3a. For heavy mass defect there appears a pronounced peak in the low frequency region which shifts further towards lower edge of the band with increase in mass. With the shift the

SIMPLE CUBIC LATTICE (ISOTOPIC DEFECT)

(a) $\frac{\Delta M}{M} = 0$ , (b) $\frac{\Delta M}{M} = -0.1$,

(c) $\frac{\Delta M}{M} = -0.5$, (d) $\frac{\Delta M}{M} = -0.8$,

(e) $\frac{\Delta M}{M} = 2$

$\omega^2/\omega_m^2 \longrightarrow$
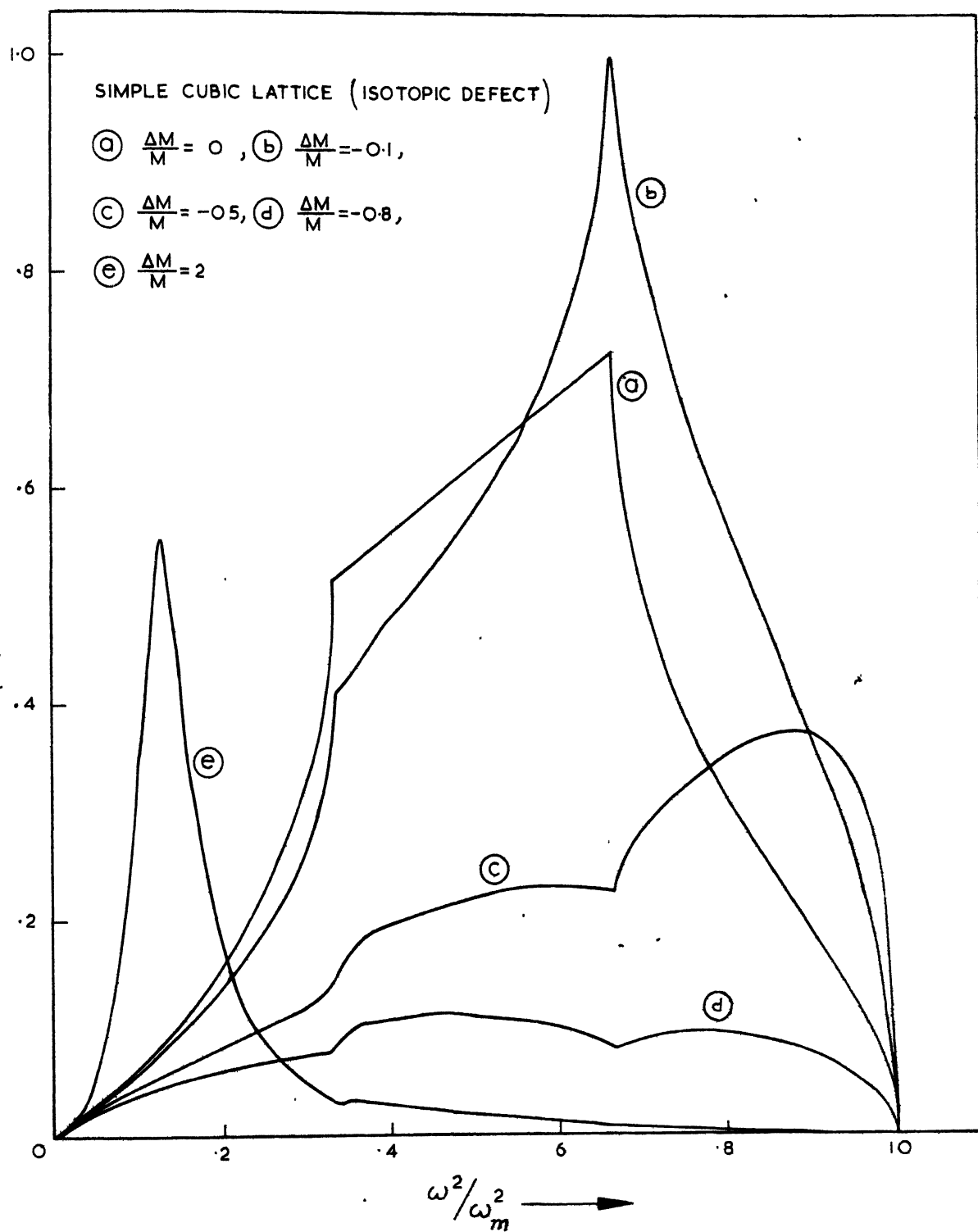
FIG 3

sharpness also increases. For very light isotopes the
absorption spectrum readjusts itself (Fig. 3c and 3d) with
localized modes appearing above the maximum frequency of the
host lattice. For an isotope defect whose mass is slightly
less than the normal atom a high frequency resonant mode
(Fig. 3b) is produced. In this case the position and shape
of the absorption line is very susceptible to the perturbat-
ion parameters. In Fig. 4 the variation of the shape and
location of the above line is shown with respect to a change
of force constant. By increasing the impurity host force
constant by 20 % the line transforms into a very well defi-
ned one at the band edge of the high frequency side. Further
increase in force constant or decrease in mass, shifts it out
of the band. A 20 % reduction in the impurity host force
constant shifts the line towards the low frequency side with
a broadening of its width. But further decrease in the force
constant the shape becomes finer and moves towards the lower
edge.

These resonances are due to the peaking ups in the
density of states as has been shown in equation (3.38b) and
pointed out first by Brout and Visscher and Takeno. This
specific mode also shows up in the thermal conductivity dip.
Inhand resonant modes for heavy mass defects or tremendous
softening in the force constant are common for all the latt-
ices we have investigated. The difference in their positions
etc. arises due to the structure of the lattices.

SIMPLE CUBIC LATTICE

(a) $\frac{\Delta M}{M} = -0.1$ , $\frac{\Delta \gamma}{\gamma} = 0.$

(b) $\frac{\Delta M}{M} = -0.1$ , $\frac{\Delta \gamma}{\gamma} = -0.2$

(c) $\frac{\Delta M}{M} = -0.1$ , $\frac{\Delta \gamma}{\gamma} = -0.2$
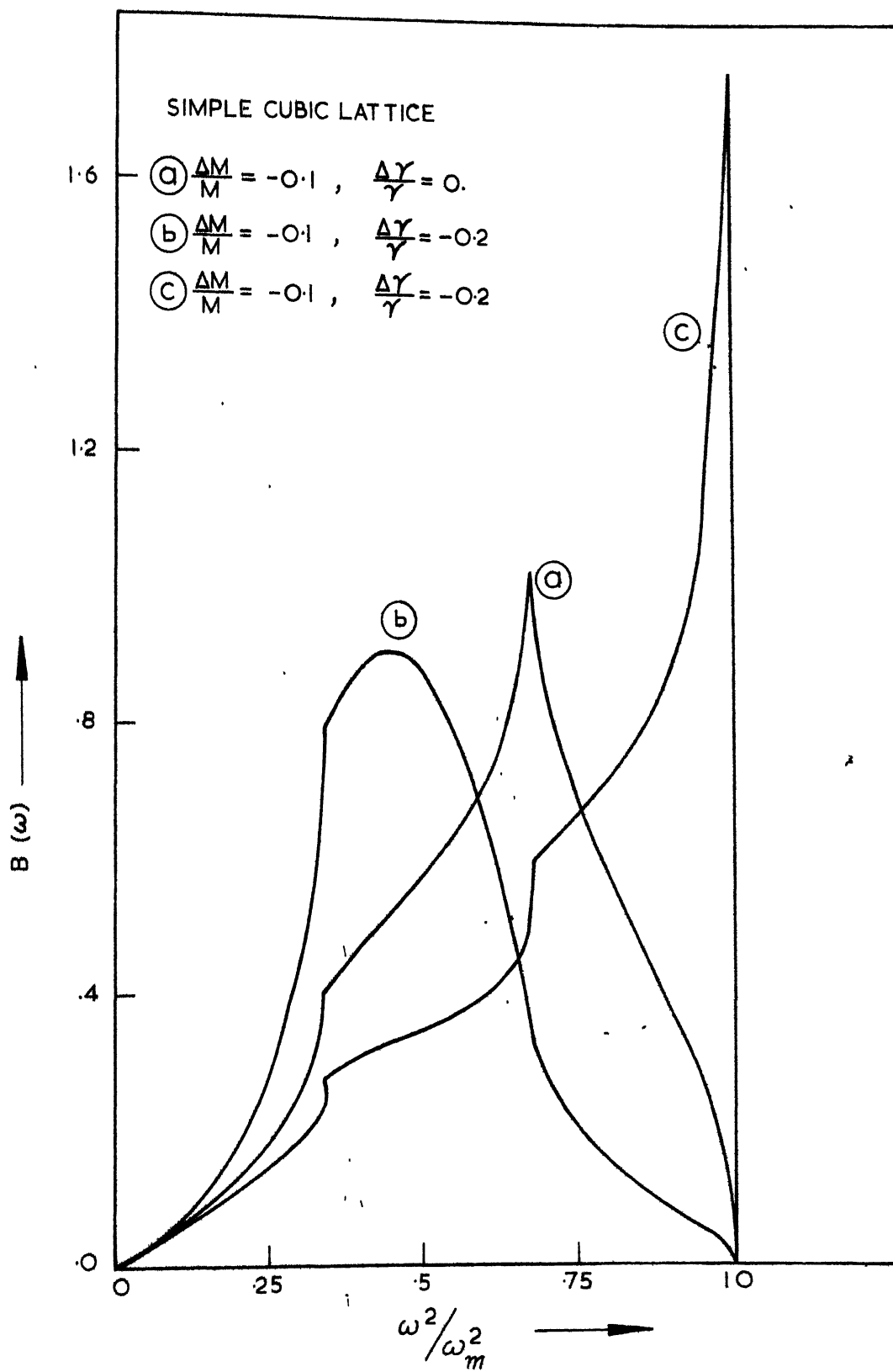
FIG.4

In case of bcc lattice model we have considered, there exists a logarithmic singularity at the mid point of the band ($\omega^2/\omega_m^2 = .5$). The unperturbed density of states goes to infinity at that point resulting zero absorption. Various absorption curves are shown in Fig. 5 and 6. Fig.5a illustrate the density of states of the unperturbed lattice. The usual sharp absorption line arises in the low frequency region (Fig. 5b) for heavy mass defect. For light isotopes (Fig. 5c) the spectrum readjusts itself. The effect of impurity host interaction is plotted in Fig. 6. The curve (Fig. 6a) illustrate the case of an isotope impurity whose mass is 90 % of that of the host atom. There are two peaks on both sides of the mid point, but the peak on higher frequency side is the stronger one. By readucing the force constant by 20 % the low frequency side peak (Fig. 6b) grows stronger with a simultaneous shift towards the lower edge, whereas the high frequency side peak gets diminished. By enhancing the force constant by 30 % the reverse effect is obtained. The high frequency side peak forms a well defined line at the band edge whereas the low frequency side absorption becomes almost flat (Fig. 6c).

The absorption line shapes for fcc lattices are not plotted as they show similar low and high frequency absorption lines. The high frequency absorption can also be achieved by a pair of sufficiently light impurities as has been shown by Takeno[119] in simple cubic lattice.

B.C.C. LATTICE

(a) $\frac{\Delta M}{M} = 0$ , $\frac{\Delta \gamma}{\gamma} = 0.$

(b) $\frac{\Delta M}{M} = 2$ , $\frac{\Delta \gamma}{\gamma} = 0$

(c) $\frac{\Delta M}{M} = -0$, $\frac{\Delta \gamma}{\gamma} = 0.$

$\omega^2 / \omega_m^2 \longrightarrow$
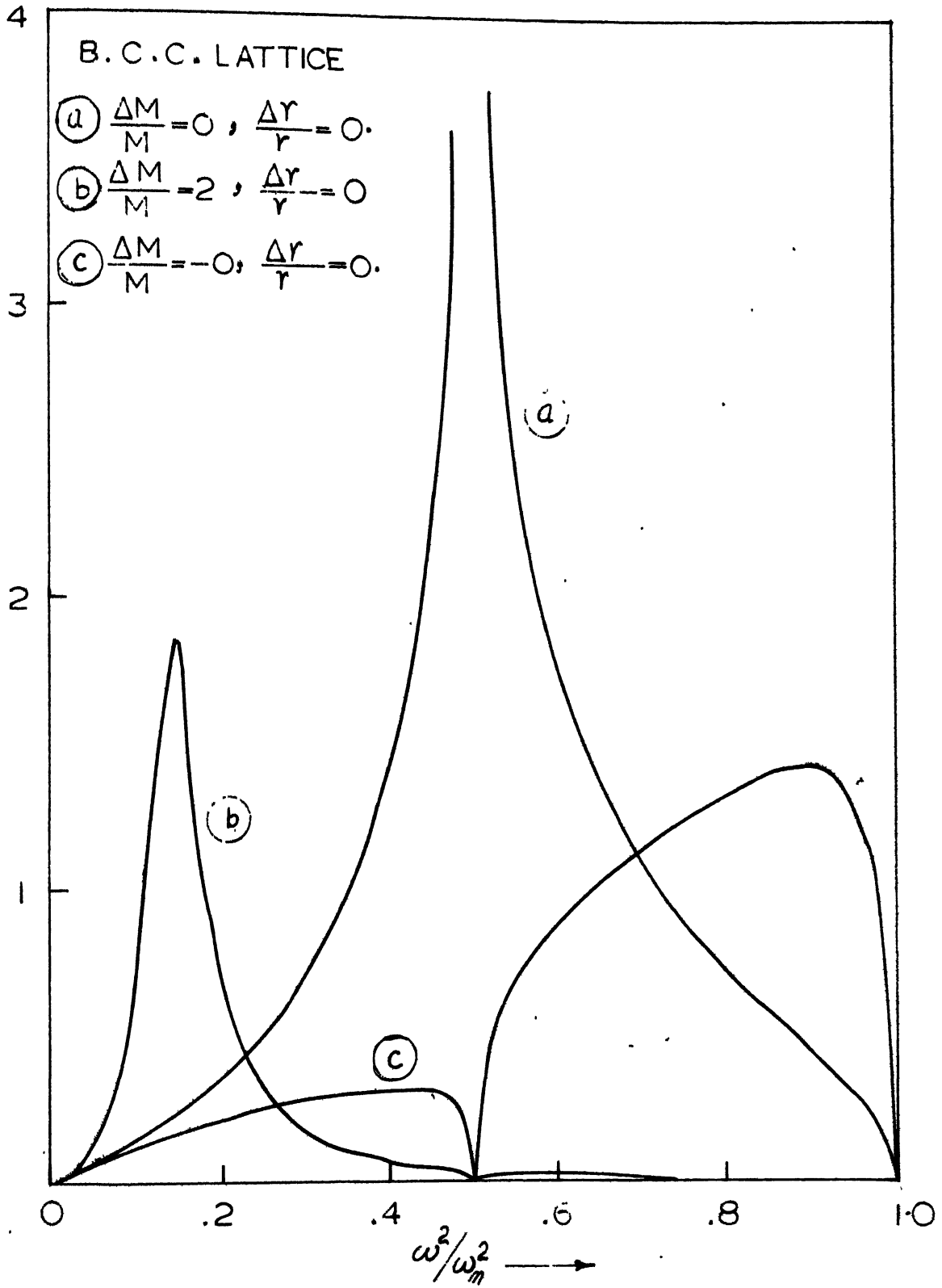
FIG. 5
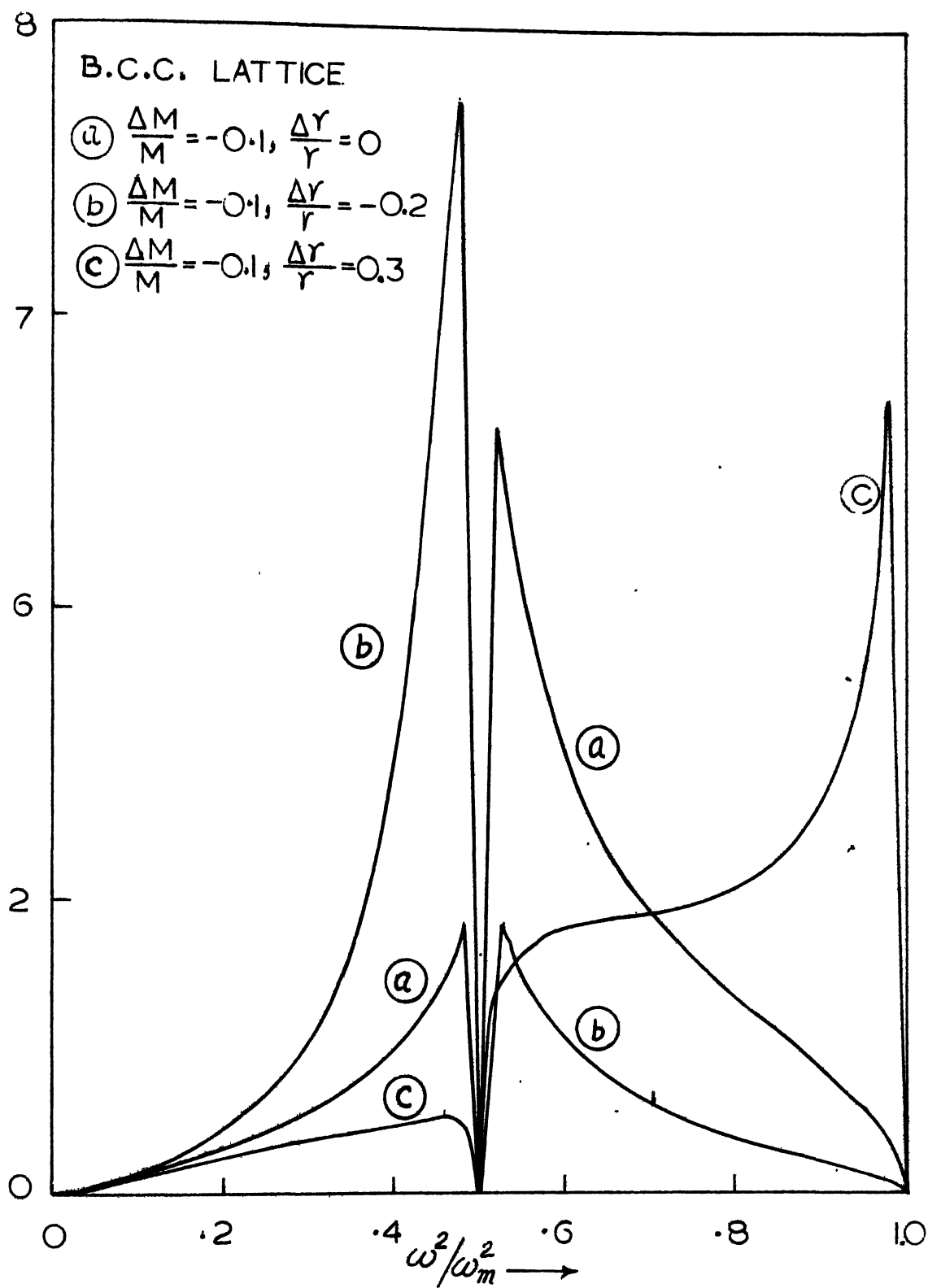
FIG. 6

# §3.4 Debye Model

Since most of the experimental observations of impurity absorption modes were detected in the very low frequency region of the frequency spectrum one can employ the isotropic Debye model to evaluate the Green's function. For a simple cubic lattice

$$\text{Re } g_{os} = - \frac{3}{M\omega_m^2} \left[ 1 + \frac{1}{2} \frac{\omega}{\omega_m} \log \left| \frac{\omega/\omega_m - 1}{\omega/\omega_m + 1} \right| \right] \quad , \qquad (3.43a)$$

$$\text{Im } g_{os} = \frac{3\pi}{2} \frac{1}{M\omega_m^2} \cdot \frac{\omega}{\omega_m} \quad , \qquad \omega < \omega_m \qquad (3.43b)$$

$$= 0 \quad , \qquad\qquad \omega > \omega_m$$

where

$$\omega_m^2 = \frac{12\gamma}{M} \quad . \qquad (3.43c)$$

For very low frequency region one can get the analytical expression for width. The resonance frequency is obtained by putting $\text{Re } D^s = 0$, and using equation (3.43a). To lowest order in $\omega^2$ this yields a solution for the resonant mode as

$$\frac{\omega_r^2}{\omega^2} \simeq \frac{\left( 1 + \frac{\Delta\gamma}{\gamma} \right)}{3 \frac{\Delta M}{M} + \frac{\Delta M}{M} \cdot \frac{\Delta\gamma}{\gamma} - 2\frac{\Delta\gamma}{\gamma}} \quad . \qquad (3.44a)$$

With the help of this value of the resonant mode frequency the width of the mode is given by

$$\Gamma(\omega_r) = \frac{3\pi}{4} \cdot \frac{\Delta M}{M} \left( \frac{\omega_r}{\omega_m} \right)^3 \omega_r^2 \quad . \qquad (3.44b)$$

Takeno and Sievers[69] have calculated these quantities to fit the experimental data in case of mixed alkali halides.

CHPATER IV

IONIC CRYSTALS

## 4.1 Lattice Model And Green's Function

In this chapter we consider the response of alkali
halide crystals (NaCl type lattice) to electromagnetic
radiation in the infrared part of the spectrum. It is a
characteristic property of ionic crystals that they have
a strong absorption in the infrared associated with the
motion of charges of opposite sign toward each other. In
the framework of harmonic theory the existence of a first
order dipole moment at zero wave vector corresponding to
the transverse optic mode (called the dispersion oscilla-
tor) is solely responsible for such a phenomena. Besides
this strong absorption maximum the experimental observation
reveals a weak continuous absorption throughout the spectrum
which arises mainly due to the anharmonicity of the crystal
potential energy. However in case of mixed alkali halides
(either anion impurities or cation impurities, sometimes
both together) the Fourier transform of dipole moment exists
for all the frequencies making the entire spectrum optically
active.

The space lattice of ionic crystal (NaCl structure)
is face centered cubic with one cation and one anion with
each lattice point. One constructs such a crystal structure

by arranging alternately the two different ions at the
lattice points of a simple cubic lattice. The features of
the model studied here are as follows. The lattice consis-
ting of N ions having masses $M_1$ and $M_2$ with charges e and
-e are situated alternately at the even and odd sites
respectively. The interaction is limited to the nearest
neighbours through equal central and noncentral forces with
force constant equal to $\gamma$. The charge distribution is
assumed to be spherically symmetric and hence the total
charge of the ion is assumed to be concentrated at the
center. This assumption implies that the charges move
rigidly without any distortion.

The impurity whose mass is $M_1 + \triangle M_1$ and nearest
neighbour force constant $\gamma + \triangle \gamma$ is situated at the origin.
This model is similar to that of Mitani and Takeno.[120] The
time independent equations of motion of the lattice are
given by

$$(M_j \omega^2 - 6\gamma)x(\underline{j}) + \gamma[x(j_1+1,j_2,j_3) + x(j_1-1,j_2,j_3) + x(j_1,j_2+1,j_3)$$

$$+ x(j_1,j_2-1,j_3) + x(j_1,j_2,j_3+1) + x(j_1,j_2,j_3-1)]$$

$$+ \sum_{\underline{j}'} P(\underline{j},\underline{j}')x(\underline{j}') = 0 . \tag{4.1a}$$

where

$$x(\underline{j}) = \text{displacement of } \underline{j}\text{-th ion,}$$

$$\underline{j} = (j_1,j_2,j_3) , \quad j = j_1 + j_2 + j_3 \quad , \tag{4.1b}$$

and

$$M_j = M_1 \delta_{j,even} + M_2\delta_{j,\ odd} \ .$$  (4.1c)

$P(\underline{j},\underline{j}')$ is the element of the usual perturbation matrix described in Chapter III. Equation(4.1a) gives two diff-erent equations with $M_1$ and $M_2$ for even and odd sites respectively. Both types can be combined into a single equation by $\acute{M}$ transformation and the resulting equation in the matrix form is

$$[(\overset{*}{M}\omega^2-\hat{A}) + \overset{\wedge}{P} ] \ \underline{U} = 0.$$  (4.2a)

with

$$\overset{*}{M}\omega^2 = [(M_1\omega^2 - 6\gamma) (M_2\omega^2 - 6\gamma)]^{\frac{1}{2}},$$  (4.2b)

$$u(\underline{j}) = (M_1\omega^2 - 6\gamma)^{\frac{1}{2}}x(\underline{j}), \text{ for } j= \text{even},$$  (4.2c)

$$= (M_2\omega^2 - 6\gamma)^{\frac{1}{2}}x(\underline{j}), \text{ for } j = \text{odd}.$$  (4.2d)

$\hat{A}$ is the usual force constant matrix for a simple cubic lattice. The new perturbation matrix $\overset{x}{P}$ is modified as

$$\overset{\wedge}{P}(\underline{j},\underline{j}') = \beta \ \overset{\wedge}{P}(\underline{j},\underline{j}'), \text{ if } j = \text{even}, \ j' = \text{even},$$  (4.3a)

$$= \frac{1}{\beta} \ \overset{\wedge}{P}(\underline{j},\underline{j}'), \text{ if } j = \text{odd}, \ j' = \text{odd}$$  (4.3b)

$$= \overset{\wedge}{P}(\underline{j},\underline{j}'), \text{ if } \ j = \text{odd}, \ j' = \text{even}$$
$$j = \text{even}, \ j' = \text{odd}$$  (4.3c)

where

$$\beta = [(M_2\omega^2 - 6\gamma)/(M_1\omega^2 - 6\gamma)]^{\frac{1}{2}}$$  (4.3d)

Now the diatomic simple cubic lattice can be treated as a monatomic cubic lattice with effective kinetic energy. The other discussion follows the same line as that of simple cubic lattice. The solution of equation(4.2a) with $\overset{\cdot\cdot}{P} = 0$ are the plane waves. So the Green's function becomes

$$\overset{..}{G}(\underline{j},\underline{j};\omega^2 - i\varepsilon) = [\overset{\wedge *}{M}(\omega^2 - i\varepsilon) - \hat{A}]^{-1}_{\underline{j},\underline{j}'}$$

$$= \frac{1}{N} \sum_{\underline{k}} \frac{e^{i\underline{k}\cdot(\underline{j}-\underline{j})}}{M\overset{*}{\omega}^2 - M\overset{..}{\omega}^2(\underline{k})-i\varepsilon} \quad . \qquad (4.4)$$

The asterisk refers to the lattice formed by the $\overset{*}{M}$ transformation. The frequency wave vector dispersion relation is obtained by solving the equation

$$\overset{\prime*}{M}\omega^2 - \overset{*}{M}\omega^2(\underline{k}) = [(M_1\omega^2-6\gamma)(M_2\omega^2-6\gamma)]^{\frac{1}{2}} + 2\gamma(\cos k_1 + \cos k_2 +$$
$$\cos k_3) = 0 \quad .(4.5)$$

The solutions are

$$\omega^2 = \tfrac{1}{2}\omega^2_m[1\pm\sqrt{1- \frac{4\sigma^2}{9(\sigma+1)^2} \; [9-(\cos k_1+\cos k_2+\cos k_3)^2]} \; ]\cdot$$
$$(4.6)$$

There exists two regions for which the frequency wave vector relationship is satisfied leaving a gap inbetween through which no wave can propagate. The upper and lower sign inside the bracket in the above equation give the optic and acoustic mode frequencies respectively. Here

$$\omega_m^2 = 6\gamma \; (M_1^{-1} + M_2^{-1}) = \omega_0^2 + \omega_a^2 \qquad (4.7a)$$

Maximum frequency of the lattice i.e.
top of the optic branch.

For $M_2 > M_1$ ,

$$\omega_0^2 = \frac{6\gamma}{M_1} = \frac{\sigma}{1+\sigma}\omega_m^2 \;\; \text{(Bottom of the optic branch)},$$
$$\qquad (4.7b)$$

$$\omega_a^2 = \frac{6\gamma}{M_2} = \frac{1}{1+\sigma}\omega_m^2 \;\; \text{(Top of the acoustic branch)},$$

and $\qquad \sigma = M_2/M_1$ . $\qquad\qquad (4.7d)$

The frequencies $\omega_a$ and $\omega_0$ get interchanged when $M_1 > M_2$ .
Here the two branches are each three fold degenerate. The
Green's functions for such crystals become wholly real inside
the gap besides the out of band regions and complex within
both the allowed bands.

## 4.2 Line Shape Function

The perturbation and Green's function matrix for the
diatomic simple cubic lattice can be treated now on the same
footing as that of the simple cubic lattice after the $M^*$
transformation. Since any physical property like that of
infrared absorption depends on the unmodified Green's funct-
ions, one has to transform them properly before making any
quantitative estimation. With the help of the transformation
equations(4.2c) and (4.2d) one can construct matrices which

transform the matrix $M\omega^2$ to $\overset{*}{M}\omega^2$ as

$$(\overset{*}{M}\omega^2 - \hat{A}) = \hat{S}'(\hat{M}\omega^2 - \hat{A})\, S^{-1} \qquad (4.8)$$

where $\hat{S}$ and $\hat{S}'$ are diagonal matrices whose elements are given by

$$\hat{S}_{j,j'} = \delta_{j,j'}[(M_1\omega^2 - 6\gamma)^{\frac{1}{2}}\delta_{j,even} + (M_2\omega^2 - 6\gamma)^{\frac{1}{2}}\delta_{j,odd}],$$

and $\qquad (4.9a)$

$$\hat{S}'_{j,j'} = \delta_{j,j'}[(M_2\omega^2 - 6\gamma)^{\frac{1}{2}}\delta_{j,even} + (M_1\omega^2 - 6\gamma)^{\frac{1}{2}}\delta_{j,odd}].$$

$$(4.9b)$$

Hence the Green's function matrix occuring in equation (2.49) of power absorption is expressed as

$$(\hat{M}\omega^2 - \hat{A})^{-1} = \hat{S}^{-1}(\overset{*}{M}\omega^2 - \hat{A})^{-1}\hat{S}', \qquad (4.10a)$$

or

$$\hat{G} = \hat{S}^{-1}\overset{*}{\hat{G}}\hat{S}'. \qquad (4.10b)$$

In case of charged impurity only one element of the perturbed Green's function is needed for calculating the absorption co-efficient. Here the entire lattice consists of ions and the sum over $j$ and $j'$ should be carried out over all the lattice sites. The charge of any ion is

$$e_j = (-1)^j e. \qquad (4.11)$$

So the absorption line shape expression becomes

$$B(\omega) = \frac{1}{2}e^2E^2\omega\, \text{Im}\sum_{j,j'}[\frac{\delta_{j,even}}{(M_1\omega^2 - 6\gamma)^{\frac{1}{2}}} - \frac{\delta_{j,odd}}{(M_2\omega^2 - 6\gamma)^{\frac{1}{2}}}]\overset{*}{G}(j,j')\,x$$

$$[(M_2\omega^2-6\gamma)^{\frac{1}{2}}\delta_{j',even}-(M_1\omega^2-6\gamma)^{\frac{1}{2}}\delta_{j',odd}] \cdot \quad (4.12)$$

The method of partitioning as discussed in Chapter III helps us to sum over $j$ and $j'$ conveniently. Here the equation (3.13) is rewritten in a slightly different form in order that the unperturbed Green's function separates out.

$$\hat{G}^* = \hat{G}^o + \hat{H}^* \hat{G}^o \quad , \quad\quad (4.13a)$$

with

$$\hat{H} = \begin{pmatrix} -\hat{g}^k p^k (I+g^* \hat{p})^{-1} & 0 & 0 & \cdots \\ -g^*_{21}\hat{p}^* (I+g^* \hat{p})^{-1} & 0 & 0 & \cdots \\ \cdot & & \cdot & \cdot & \cdots \end{pmatrix} \quad . \quad (4.13b)$$

Now substituting the first term of equation(4.13a) in the expression for power absorption and making use of the explicit form of the Green's function, the summation over all the lattice sites can be done easily. The contribution of perfect crystal to infrared absorption has the following form

$$B_p(\omega) = \frac{1}{4} Ne^2E^2\omega \left( \frac{M_1+M_2}{M_1M_2} \right) \, Im \, \frac{1}{\omega^2-\omega_m^o-i\varepsilon}$$

$$= \frac{\pi}{4} Ne^2E^2\omega\left(\frac{M_1+M_2}{M_1M_2}\right) \, \delta \, (\omega^2-\omega_m^2) \, . \quad\quad (4.14)$$

The $\delta$-function shape of the absorption is the well known phenomenon in ionic crystals. In case of perfect crystals there appears a continuum of weak absorption with a strong well defined maximum at the transverse optic mode

frequency. The continum arises due to anharmonicity terms or the higher order dipole moment of the crystal. But these processes involves more than one phonon and bring temperature dependence to the absorption. Both these processes are similar except one fundamental difference.

Although a continuous absorption spectrum is obtained due to higher order dipole moment the infinitely strong absorption or the $\delta$-function behaviour is reduced only by the anharmonicity which couples the phonon giving a finite life time of this mode to decay into the neighbouring modes.

On the otherhand the defect also relaxes the selection rules producing absorption at all frequencies. In the harmonic approximation the dispersion oscillator predominates in its neighbourhood. Any defect-activated mode arising in that region will be difficult to distinguish. Only these modes which lie far away from the Reststrahl region can be studied properly. This makes the impurity resonant modes in the acoustic branch much more amenable to experimental study than those inside the optic branch.

The second term of equation(4.13a) is the contribution of the impurity to infrared absorption. When $\hat{H}\hat{G}^{0*}$ is substituted in equation(4.12) the summation over $\underline{j}'$ is carried out easily, because it occurs in the exponential in the integrand of the integrals for the element of $\hat{G}^{0*}$. The structure of $\hat{H}$ matrix as given by equation(4.13b) is such

that it has non vanishing elements only upto column whose index corresponds to the last lattice site affected by the impurity. This enables us to write the impurity absorption as

$$B_I(\omega) = \tfrac{1}{2} e^2 E^2 \omega \, \text{Im} \, \frac{1}{4a} \Big[ \frac{(M_1+M_2)\omega^2 - 12\gamma + 2a}{a - 6\gamma} \sum_{j\mu'} e^{i(j+\mu')\pi} \hat{H}_{j,\mu'} + \frac{(M_1+M_2)\omega^2 - 12\gamma - 2a}{a + 6\gamma} \sum_{j,\mu'} H_{j,\mu'}$$

$$+ \frac{(M_2-M_1)\omega^2}{a + 6\gamma} \cdot \sum_{j,\mu'} e^{ij\pi} H_{j,\mu'} + \frac{(M_2-M_1)\omega^2}{a-6\gamma} \sum_{j,\mu'} e^{i\mu'\pi} H_{j,\mu'} \Big]$$

$$(4.15)$$

where $\mu'$ runs over all the affected lattice sites and a is given by

$$a = [(M_1\omega^2 - 6\gamma)(M_2\omega^2 - 6\gamma)]^{\frac{1}{2}} \qquad (4.16)$$

The sum over j can be performed by making use of the partitioned form of H. For example the first term in the above equation becomes

$$\sum_{j,\mu'} e^{i(j+\mu')\pi} H_{j,\mu'} = - \sum_{n,\mu,\mu_1,\mu'} (g_n^*)_{\mu\mu'} [p^*(I + g^* p^*)^{-1}]_{\mu,\mu'}$$

$$\times e^{i(n+\mu+\mu')\pi} \cdot (4.17)$$

where $j = n + \mu$ and $n$ runs over all the centers of the partitioned blocks of the Green's function matrix. By using the explicit formula for the element of $g_n^*$ the sum is carried over $n+\mu$ and the result is obtained in the following form

$$\sum_{\overline{j,\mu'}} e^{i(j+\mu)\pi} \hat{H}_{\underline{j},\underline{\mu}'} = - \frac{1}{a-6\gamma} \sum_{\underline{\mu},\underline{\mu}'} [\hat{p}^* (\hat{I}+\hat{g}\hat{p})^{-1}]_{\underline{\mu},\underline{\mu}'} e^{i\pi(\mu+\mu')}$$

$$(4.18)$$

The other terms of equation (4.15) can be simplified in the similar manner to give

$$B_I(\omega) = -\tfrac{1}{2} e^2 E^2 \omega \, \mathrm{Im} \, \frac{1}{4a} \Big[ \frac{(M_1+M_2)\omega^2-12\gamma+2a}{(a-6\gamma)^2} \sum_{\underline{\mu},\underline{\mu}'}$$

$$[\dot{p}^* (\dot{I}+\ddot{g}^* \dot{p})^{-1}]_{\underline{\mu},\underline{\mu}'} e^{i\pi(\mu+\mu')} + \frac{(M_1+M_2)\omega^2-12\gamma-2a}{(a+6\gamma)^2} \sum_{\underline{\mu},\underline{\mu}'}$$

$$[\hat{p}(\hat{I}+\hat{g}^* \hat{p})^{-1}]_{\underline{\mu},\underline{\mu}'} + \frac{(M_2-M_1)\omega^2}{a^2-36\gamma^2} \sum_{\underline{\mu},\underline{\mu}'} [\hat{p}^* (\hat{I}+\hat{g}^* \hat{p})^{-1}]_{\mu\mu'}$$

$$(e^{i\pi\mu} + e^{i\pi\mu'})\Big] . \qquad\qquad (4.19)$$

Now the sum extends only to those lattice sites which are affected by the impurity and the total number is limited in this case to seven. Instead of summing directly over $\mu$ and $\mu'$ we adopt the following procedure so that the result can be expressed in a more convenient form. The symmetry of the defect lattice and the $\hat{V}$ matrix which block diagonalizes the submatrix $(\hat{I}+\hat{g}^*\hat{p})$ were discussed in Chapter III. Here the same $\hat{V}_s$ matrix can block diagonalize the matrix $\hat{p}^* (\hat{I}+\hat{g}^*\hat{p})^{-1}$ into its various irreducible parts. Then the summation over $\mu$ and $\mu'$ is carried out for each partial wave blocks. The various sums that occur in the above equation are

$$\sum_{\underline{\mu},\underline{\mu}'} [\dot{p}^{*}(\hat{I}+\hat{\dot{g}}^{*}\hat{p})^{-1}]_{\underline{\mu},\underline{\mu}'} \, e^{i\pi(\mu+\mu')} = \frac{1}{D^{*S}} (R-Q+6S), \qquad (4.20a)$$

$$\sum_{\underline{\mu},\underline{\mu}'} [\hat{p}^{*}(\hat{I}+\hat{\dot{g}}\,\hat{p})^{-1}]_{\underline{\mu},\underline{\mu}'} = \frac{1}{D^{*S}} (R+Q+6S), \qquad (4.20b)$$

$$\sum_{\underline{\mu},\underline{\mu}'} [\dot{p}^{*}(\hat{I}+\dot{g}^{*}\dot{p}^{*})^{-1}]_{\underline{\mu},\underline{\mu}'} e^{i\pi\mu} = \sum_{\underline{\mu},\underline{\mu}'} [p^{*}(I+\hat{g}\dot{p})^{-1}]_{\underline{\mu},\underline{\mu}'} e^{i\pi\mu'} = \frac{1}{D^{*S}}(R-6S).$$
$$(4.20c)$$

where

$$R = \not{b}[\alpha+\triangle M_{1}\omega^{2} \frac{\triangle\gamma}{\gamma} (M_{1}\omega^{2}-6\gamma)g_{1}^{*}] \quad , \qquad (4.21a)$$

$$Q = 12\triangle\gamma \, (1+\triangle M_{1}\omega^{2}g_{1}^{*}) \quad , \qquad (4.21b)$$

$$S = - \frac{\triangle\gamma}{\beta} \, (1+\triangle M_{1}\omega^{2}\beta g_{0}^{*}) \quad . \qquad (4.21c)$$

and

$$D^{S}=1+ \frac{\triangle\gamma}{\gamma}+ \frac{\triangle\gamma}{\gamma}(1+\frac{\triangle M_{1}}{M_{1}}) \frac{M_{1}\omega^{2}}{6\gamma} + \beta M_{1}\omega^{2}g_{0}^{*}[ \frac{\triangle M_{1}}{M_{1}}(1+ \frac{\triangle\gamma}{\gamma})- \frac{\triangle\gamma}{\gamma} \cdot$$

$$(1+ \frac{\triangle M_{1}}{M_{1}}) \frac{M_{1}\omega^{2}}{6\gamma} ] . \qquad (4.21d)$$

Here $D^{*S}$ is the s-wave part of the determinant $|\hat{I}+\hat{\dot{g}}^{*}\dot{p}^{*}|$ . The sum over the other two types of modes vanishes indentically. So the infrared absorption takes place only through the totally symmetric mode in ionic crystals and is similar to the other cases discussed in Chapter III. The physical picture for such phenomena is as follows.

The p and d-like modes involve the motions of the

nearest neighbours of the impurity. For ionic crystals they carry similar charges but move in such a way that the resulting dipole moment associated with these modes vanishes. For example in p-like motion (Fig. 2b) a pair of ions on both sides of the impurity move in opposite directions by the same amplitude cancelling each other's dipole moment.

In d-type motion (Fig. 2c) either all the six or four of the nearest neighbours take part in the vibration. For the first case four of the atoms move in one direction and the remaining two move in opposite directions with amplitudes twice as that of the others. In second case two of the atoms move in one way forming a pair and the other pair moves in the opposite direction. The resulting dipole moment in each of those cases become zero. Hence these modes cannot be excited by the infrared even in the ionic crystals. The possibility of exciting other modes by the infrared will arise if the charge symmetry in the surrounding atoms near the impurity is destroyed. The process of direct calculation cannot reveal the physical situation as clearly as discussed above.

So finally the absorption formula reduces to

$$B_I(\omega) = \tfrac{1}{2} e^2 E^2 \omega \, \text{Im} \, \frac{N}{D^{s*}} \quad . \qquad (4.22)$$

where

$$N = -\frac{1}{M_2(\omega^2-\omega_m^2)^2}\left[\left(\frac{\Delta M_1}{M_1}\right)\omega^2\sigma+\frac{\Delta\gamma}{\gamma}\frac{(\sigma+1)^2}{\sigma}\omega_0^2-(1+\sigma)\left(\frac{\Delta M_1}{M_1}\right)\right.$$

$$\left.\left(\frac{\Delta\gamma}{\gamma}\right)\frac{\omega^2}{\omega_m^2}(\omega^2-\omega_m^2-\omega_a^2)+a(1+\sigma)\left(\frac{\Delta M_1}{M_1}\right)\left(\frac{\Delta\gamma}{\gamma}\right)\frac{\omega^2}{\omega_m^2}(\omega^2-\omega_m^2-\omega_a^2)\overset{*}{\hat{g}}_0\right].$$

$$(2.23)$$

In deducing the above expression the following Green's function relationships (similar to those of the simple cubic monatomic lattice) have been used.

$$a\hat{g}_0 + 6\gamma\overset{*}{g}_1 = 1 , \qquad (2.24a)$$

$$ag_1^* + \gamma(g_0^* + 4g_{11}^* + g_2^*) = 0. \qquad (2.24b).$$

## 4.3 Density Of States

The squared distribution function of frequency is given by

$$f(\omega^2) = \frac{Im}{N\pi}Tr(\hat{M}\hat{G}) = \frac{Im}{N\pi}Tr(\hat{M}^*\hat{G}), \qquad (2.25)$$

where

$$\hat{M}' = \hat{S}'\hat{M}\hat{S}^{-1}. \qquad (2.26)$$

Equation(2.25) can be written as

$$f_0(\omega^2)+\Delta f(\omega^2) = \frac{Im}{N\pi}[Tr\overset{*}{M}{}^0\hat{G}{}^0+\Delta M_1\beta\overset{*}{G}(0,0)$$

$$-Tr\overset{*}{M}{}^0\hat{G}{}^0\hat{P}{}^*(\hat{I}+\hat{G}{}^0\overset{*}{P})^{-1}\hat{G}{}^0] .(2.27)$$

where $f(\omega^2)$ is the density of states for the unperturbed lattice and is given by

$$\rho(\omega^2) = \frac{Im}{N\pi} \, Tr(\hat{M}^o \hat{G}^o) = \frac{Im}{2\pi} \, (M_1\beta + \frac{M_2}{\beta}) g_o^* \qquad (2.28)$$

Hence the change in the density of states is given by

$$\rho(\omega^2) = \frac{Im}{N\pi} \, [ \, \Delta M_1 \beta \hat{G}^*(\underline{0},\underline{0}) - Tr \, \hat{M}^o \hat{G}^o \hat{P}^- (\hat{I} + \hat{G}^o \hat{P}^*)^{-1} \hat{G}^o ]$$

$$= \frac{Im}{N\pi} \, [\cdot M_1 \beta \, \hat{G}^*(\underline{0},\underline{0}) + \tfrac{1}{2}(\beta M_1 + \frac{M_2}{\beta}) Tr \hat{G}^o \hat{P}^*(\hat{I} + \hat{G}^o \hat{P}^*)^{-1}$$

$$- \tfrac{1}{2}(\beta M_1 - \frac{M_2}{\beta}) Tr \, \hat{R}^- \hat{P}^* ( \, \hat{I} + \hat{G}^o \hat{P}^*)^{-1}]. \qquad (2.29)$$

where we have used the following relationships.

$$M_{\underline{i},\underline{i}'} = \tfrac{1}{2} \, \delta_{\underline{i},\underline{i}'} [ (\beta M_1 + \frac{M_2}{\beta}) + (\beta M_1 - \frac{M_2}{\beta}) \, e^{ij\pi} ] \, ,$$

$$\qquad (2.30a)$$

$$\sum_n G^o(\underline{i},\underline{n}) G^o(\underline{n},\underline{i}) = - \frac{d}{da} \, G^o(\underline{i},\underline{i}') = - \, G^{o'}(\underline{i},\underline{i}) \, , (2.30b)$$

and

$$R(\underline{i},\underline{i}') = \sum_n G^o(\underline{i},\underline{n}) G^o(\underline{n},\underline{i}') \, e^{in\pi} = \frac{1}{2a} \, G^o(\underline{i},\underline{i}') [(-1)^j$$

$$+ (-1)^j] \, . \, (2.30c)$$

The traces of the matrices occuring in equation(2.29) can
be evaluated in the following way. The second trace is
easily calculated by the use of the partitioned form of
their respective matrices which reduce the dimensionality
of the resultant matrix i.e.

$$Tr \, \hat{R}^* \hat{P}^* (\hat{I} + \hat{G}^o \hat{P}^*)^{-1} = Tr \, r^* p^* (\hat{I} + \hat{g}^* \hat{p}^*)^{-1}. \qquad (2.31)$$

where $\dot{r}$ is the first block of the partitioned $\hat{R}^*$ matrix. Then one can calculate the trace with the help of the group theoretic block diagonalization procedure. The other trace is expressed as

$$\text{Tr } \hat{G}^{*0}\hat{P}^{*} (\hat{I} + \hat{G}^{0}\hat{P}^{*})^{-1} = \text{Tr } \frac{d}{da} \log (\hat{I} + \hat{G}^{0}\hat{P}^{*}) - \text{Tr } \hat{G}^{*0}\frac{d\hat{P}^{*}}{da}$$

$$= \text{Tr } \frac{d}{da} \log (\hat{I} + \hat{G}^{0}\hat{P}^{*}) - [\ \frac{\alpha}{2a}\ \frac{6\gamma(M_1-M_2)}{(M_1\omega^2-6\gamma)} + \beta\Delta M_1$$

$$+ \frac{\Delta\gamma}{2a}\ \frac{6\gamma(M_2-M_1)}{(M_2\omega^2-6\gamma)}]\ \times\ G^{*}(\underline{0},\underline{0})/\tfrac{1}{2}(\beta M_1 + \frac{M_2}{\beta})$$

$$+ \frac{\Delta\gamma}{2a}[\ \frac{6\gamma(M_2-M_1)}{(M_2\omega^2-6\gamma)} -/\ \tfrac{1}{2}(\beta M_1 + \frac{M_2}{\beta})]\sum_{\mu}' G(\underline{\mu},\underline{\mu}). \quad (2.32)$$

where

$$\sum_{\mu}' G^{*}(\underline{\mu},\underline{\mu}) = \text{Tr } (\hat{I} + \hat{g}^{*}\hat{p}^{*})\ \hat{g}^{*}\ , \qquad (2.33a)$$

and

$$G^{*}(\underline{0},\underline{0}) = (g_0^{*} + \frac{1}{\beta}\ \frac{\Delta\gamma}{\gamma}\ g_1^{*})/\ D_s^{*}\ . \qquad (2.33b)$$

Now substituting equation(2.31) and equation(2.32) in equation(2.29) and by making use of the explicit forms for equations(2.33,2.31), the change in the distribution function for the squared frequencies is expressed in a convenient form as

$$\Delta\rho(\omega^2) = \frac{\text{Im}}{N\pi} \text{Tr } \frac{d}{da} \log (\hat{I} + \hat{G}^{0}\hat{P}^{*})$$

$$= \frac{\text{Im}}{N\pi} \frac{d}{da} \log \text{Det} (\hat{I} + \hat{g}^{*}\hat{p}^{*})$$

$$= \frac{Im}{N\pi} [ \frac{D^{s'}}{D^s} + 3 \frac{D^{p'}}{D^p} + 2 \frac{D^{d'}}{D^d} ] . \qquad (3.34)$$

where

$$| I + g^* p^x | = D^{*s} D^{*3}_p D^{*2}_d , \qquad (2.35a)$$

and

$$D^p = 1 - \frac{4\gamma}{\beta} ( g^*_0 - g^*_2 ) , \qquad (2.35b)$$

$$D^d = 1 - \frac{4\gamma}{\beta} ( g^*_0 + g^*_2 - 2g^*_{11} ) . \qquad (2.35c)$$

### 4.4 Discussion

The Green's functions for the diatomic simple cubic lattice can be expressed in terms of the Green's functions of the monatomic simple cubic lattice for which extensive tables are available and hence, the absorption line shape function can be plotted for various values of impurity parameters. The denominator $D^{*s}$ is real inside the forbidden gap besides the out of band region and the poles lying in those regions give the gap and local modes respectively. This local mode frequency when arises due to hydrogen impurity in alkali halide crystals is known as U-center and were observed in the optical absorption experiments as they are infrared active.

Inside the band $D^{*s}$ is complex and the poles of its real part may lie either inside the acoustic or inside the optic branch depending on the perturbation parameters ($\frac{\triangle M_1}{M_1}$ , $\frac{\triangle\gamma}{\gamma}$) and the masses of the atoms constituting the

lattice. As regards the acoustic branch is concerned one gets the usual low frequency resonances for heavy mass defects or for impurity atoms associated with softening of nearest neighbour force constants. This behaviour is exactly similar to that of monatomic lattices. But inside the optic branch things happen in a altogether different way depending on the masses $M_1$ and $M_2$. For $M_2 > M_1$ and the substitutional impurity replacing $M_1$ one gets resonances when the mass of the impurity is less than that of the host atom. As the mass of the impurity decreases this resonance frequency shifts towards the top of the optic band and a further decrease in the mass shifts the mode out of the band and the localized mode is formed. Here the impurity host nearest neighbour force constant plays the usual role i.e. decrease of force constant lowers the resonance frequency. For $M_1 > M_2$ the light defect at $M_1$ site produces resonance which moves towards the bottom of the optic branch with decrease of mass of the impurity. The effect of force constant is also reverse here because an increase of nearest neighbour force constant lowers the resonance frequency. In case of resonances in optic branch, one faces the difficulty to study the line shapes theoretically as the Reststrahln absorption predominates and this has been pointed out earlier. However, one can estimate the nearest neighbour interaction from the infrared measurements which are either in the acoustic or in the outofband region of the frequency spectrum.

The first experimental evidence of impurity acti-
vated inband resonant modes in mixed alkali halides were
observed by Sievers[68]. He has observed a strong absorption
line in the far infrared region (at $33.5 cm^{-1}$) of the
electromagnetic spectrum in KBr:AgBr crystals (silver
concentration is of the order of $10^{18}$ per $cm^3$). Similar
observations were made by him for KCl:AgCl and KI:AgI. His
subsequent study[69] of different impurities in KBr was
striking in the sense that he could detect a very low
frequency impurity mode due to light impurities like $Li^{6,7}$.

Simple mass defect approximation in all these cases
cannot explain the results. Sievers and Takeno analysed the
KBr:LiBr spectra on the basis of a simple cubic monatomic
lattice with the defect as the only charged atom in the
crystal and employing Debye approximation for the evaluation
of the Green's function. They could obtained a fit by vary-
ing the force constant parameter. It required an enormous
reduction of impurity host force constant to obtain the
observed resonance frequency in the low frequency region.
Here we have fitted our results to their experimental data
for KBr crystal with $Li^{6,7}$ and Ag impurities. The absorpt-
ion line shapes for KBr:$Li^{6,7}$ and KBr:Ag are plotted in
Fig. 7. Table No. 1 gives the experimental data on the
resonance frequencies and the values obtained for the force
constant parameter ($\frac{\Delta\gamma}{\gamma}$). The results on the basis of a
simple cubic lattice with a charged impurity are also given

DIATOMIC SIMPLE CUBIC LATTIC

(a) KBr : Li$^7$Br

(b) KBr : Li$^6$Br

(c) KBr : Ag$^{108}$Br

$\omega/\omega'_M \longrightarrow$
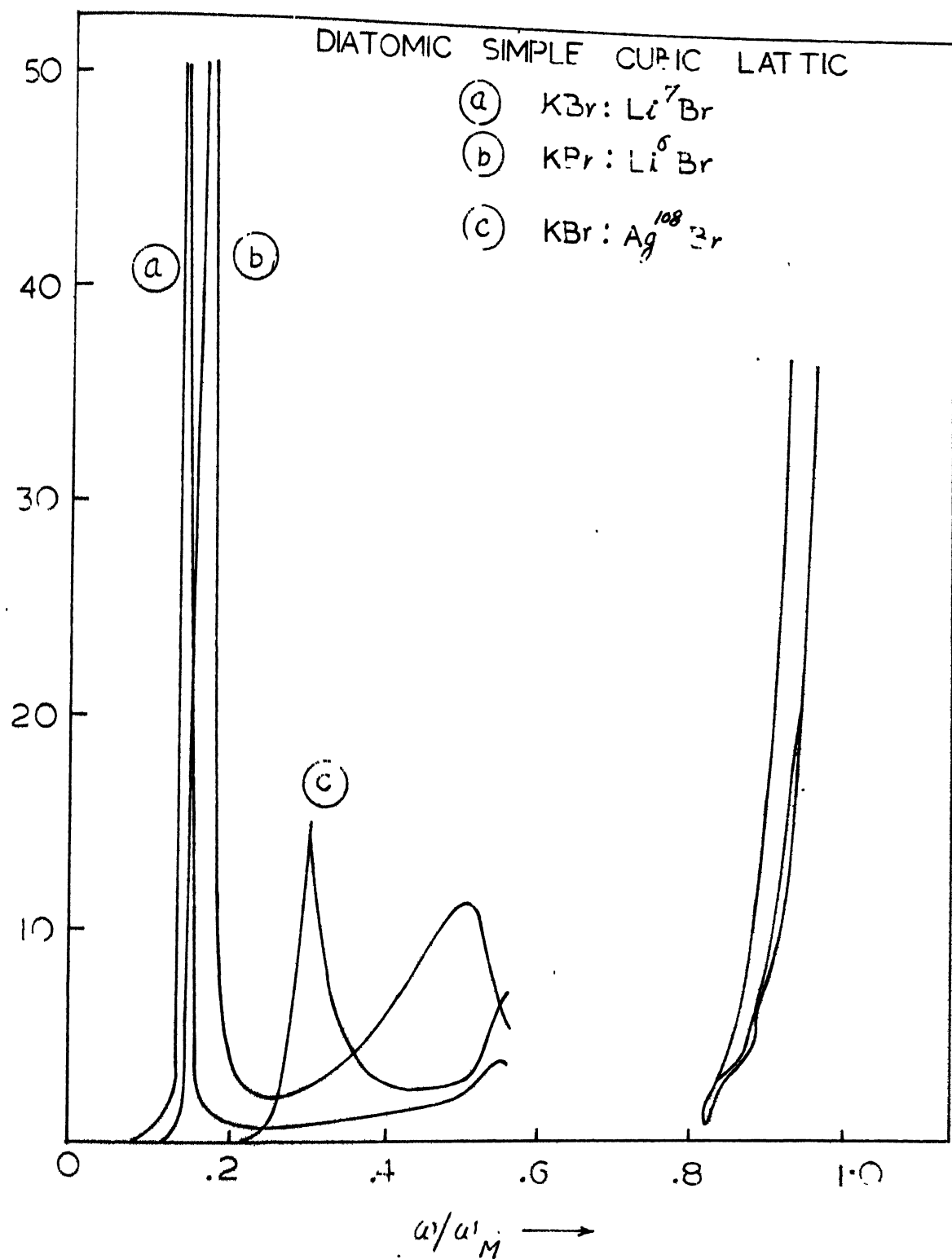
Table No. 1

Resuls for various infrared impurity lines in KBr

| Systems | $V_1/M_1$ | Observed resonance frequency in cm⁻¹ | $\omega/\omega_m$ | ΔY/Y calculated (Diatomic simple cubic lattice) | ΔY/Y calculated (Monatomic simple cubic lattice) |
|---|---|---|---|---|---|
| KBr:Li$^6$Br | −0.846 | 17.9 | .158 | −0.994 | −0.994 |
| KBr:Li$^7$Br | −0.820 | 16.3 | .144 | −0.995 | −0.995 |
| KBr:AgBr | 1.770 | 33.5 | .296 | −0.594 | −0.46 |

for comparision.

Other relevant data for potassium bromide crystal.

(i) Mass of potassium ion = 39.1 amu

(ii) Mass of bromine ion = 79.9 amu

(iii) $\sigma = M_2/M_1 \sim 2$

(iv) Wavelength of maximum absorption = 88.3 $\mu$.

The results for Li[6,7] are in agreement with that of Sievers and Takeno who had utilized the Debye model. Since the electromagnetic radiation excites the impurity inband modes in these systems at long wavelengths the details of the structure of the lattice become less important. For such frequencies the difference of masses of both the ions seems insignificant. This is primarily the reason one gets almost identical results for the force constant parameters in KBr:Li by treating the lattice as monatomic simple cubic. But there is a noticeable difference of the two models for KBr:Ag. This makes it possible to use a Debye model calculation for low frequency resonances. For higher frequency this model becomes inaccurate.

From the above analysis of experimental and theoretical situations of infrared absorption in mixed alkali halides certain inferences concerning the impurity host interaction can be made. There is a remarkable softening of impurity host interaction for small ions like $Li^+$ in KBr and KCl. Thermal conductivity[121,122] measurements at low

temperatures show dips indicating resonance scattering of phonons at very low frequencies. The specific case of $Li^+$ impurities in KCl and KBr were widely studied in order to determine the impurity configuration in the host lattice.

Besides the thermal conductivity and infrared absorption other experimental observations like that of the electrocaloric[123] and dielectric[124] measurements indicate a peculiar type of lattice distortion that arises when the size of the impurity ion is much smaller compared to the size of the host ion it replaces. Particularly this is so in case of $Li^+$ impurities in potassium halides where the volume of the potassium cavity is nearly 8 times larger than that of the lithium (the radius of $K^+ = 1.33A^o$, the radius of $Li = .68A^o$). These experiments suggest that instead of the normal lattice site as the equilibrium position, the $Li^+$ has a number of equivalent off site positions and it tunnels between these equilibrium positions. In this respect the behaviour of $Li^+$ ion is similar to that of the molecular impurities ($CN^-$, $NO_2^-$, $OH^-$) when substituted in the crystal. The dipole moment, polarizability in case of monatomic impurities arise due to its off center positions whereas the molecular impurities possess them intrinsically due to their internal modes.

The earliest theoretical investigation concerning this central instability was carried out by Mathew[125]. He

has calculated the energy of the impurity by taking into account the coulomb, repulsive and electronic polarization terms and observed minima for $Li^+$ in KCl along $\langle 100 \rangle$ directions. Dienes et al[126] performed a more elaborate calculation which supported the multiwell shape for the potential well. Bowen, Gomez and Krumhansl[127,128] have extended it further by assuming a three dimensional model potential having the octahedral symmetry which may have 6 wells along $\langle 100 \rangle$, 8 well along $\langle 111 \rangle$ and 12 wells along $\langle 110 \rangle$ directions. By making use of the LCAO method and group theory they have calculated the ground state splitting due to the tunnelling motions and some of the experimental data were fitted to the various transitions.

The multiwell shape of the potential inside the cavity is a valid description for small ions. For other impurities like that of Ag (ionic radius of $Ag^+ = 1.26A^0$) the matching is more or less balanced and the usual description of the substitutional defect holds good.

# CHAPTER V

## DEBYE-WALLER FACTOR

In this Chapter we shall discuss briefly the
dynamics of an individual atom in connection with the
Mössbauer effect. In most cases of resonant emession or
absorption of $\gamma$-rays by nuclei bound in a crystal the
emitting or the absorbing nucleus happens to be an impur-
ity embedded in the crystal and hence in analysing the
results for such cases the effect of impurity on the lattice
vibrations of the host crystal should be taken into consi-
deration.

The probability that a resonant $\gamma$-ray emission
or absorption will take place without creation or destru-
ction of a lattice vibrational quantum of energy is known
as 'Debye-Waller factor' in analogy with the corresponding
factor which determines the intensity of the scattering
of x-rays or neutrons in crystals. This probability factor,
its temperature variation and the temperature dependence
of second order Doppler shift of the zero phonon line are
directly related to the dynamics of the resonant nucleus.
Since the Mossbauer active nucleus is a foreign atom in
the crystal, its interaction with the host may be different
from that between the host atoms and so the dynamics
depends significantly in some cases on this parameter
besides the mass difference. This makes it possible to

utilize Mossbauer effect as a tool for estimating impurity host force constant.

By general arguments of momentum conservation and translational invariance Lipkin[129] has shown that the relative probability of a $\gamma$-ray emission or absorption which accompanied by a transition of the crystal state from $|E_i\rangle$ to $|E_f\rangle$ is given by the matrix element

$$P(E_f, E_i) = \left| \left\langle E_f \right| e^{i\underline{K} \cdot \underline{R}(\underline{i})} \left| E_i \right\rangle \right|^2 \quad . \quad (5.1)$$

where $\underline{K}$ is the wave vector of the $\gamma$-ray and $\underline{R}(\underline{i})$ is the instantaneous position vector of the resonant atom. Since it is assumed that the crystal state is unchanged during this process, the probability is determined by $P(E_i, E_i)$. But the initial state is quite arbitrary and so this probability should be averaged over an equilibrium distribution of initial states i.e.

$$f = \left\langle P(E_i, E_i) \right\rangle = \frac{\sum_i e^{-\beta E_i} \left| P(E_i, E_i) \right|^2}{\sum_i e^{-\beta E_i}} , \quad (5.2)$$

The evaluation of this averaged quantity has been discussed by Van Hove.[130] For harmonic crystals this is directly related to the mean square displacement of the impurity as

$$f = e^{-K^2 \left\langle u^2(\underline{i}, 0) \right\rangle} \quad . \quad (5.3)$$

The exponent of the Debye-Waller factor gets

changed if the anharmonicity is taken into account. But the most dominant factor is still given by the above expression. Evaluation of $\langle u^2(j,0) \rangle$ has been achieved in various ways taking into consideration the lattice models for host crystals. Most of the calculations were performed for Debye-solids with an effective Debye-temperature i.e.

$$\langle u^2 \rangle = \frac{3}{4mk\Theta_f} \left[ 1 + \left(\frac{T}{\Theta_f}\right)^2 \int \frac{x\,dx}{e^x - 1} \right] . \qquad (5.4)$$

where the effective Debye-temperature is given by

$$\Theta_f = \Theta_D \left( \frac{M}{M'} \cdot \frac{\gamma'}{\gamma} \right)^{\frac{1}{2}} . \qquad (5.5)$$

Here the impurity parameters enter into the calculation through the effective Debye-temperature. From the experimental value of Debye-Waller factor one can estimate the effective Debye temperature and hence the impurity host nearest neighbour interaction. Bara et al[131] have measured Debye-Waller factor for $Fe^{57}$ in sixteen different host crystals and came to the conclusion that the binding between the impurity and host remains the same as that between the host atoms. Recently Musshaur[132,133] et al have studied the same problem in some of the above hosts like that of platinum, palladium, and copper for a wide range of temperatures and they could obtain a good fit by assuming the simplified model of an Einstein crystal with an effective Einstein temperature. The force constant was seen to increase by 20 % in case of platinum and palladium and 20 % less in case of copper.

This suggests the possibility of estimating the

impurity host force constant by taking suitable models
for the host crystals. The models in lattice dynamical
calculations are difficult to handle as they demand compli-
cated numerical work. Here we use the scalar models as
has been discussed in earlier Chapters to fit up some of
the available data and estimate the change in the nearest
neighbour interaction. This calculation, though based on
an unphysical model, is presented here to throw some light
on the nature of the computational problems arising in
the process.

The impurity is assumed to be at the origin of
the co-ordinate system. Using the time independent displ-
acement into correlation functions as given by equation
(2.47b) the mean square displacement of the impurity is
given by

$$\left\langle u^2(\underline{0},0) \right\rangle = \lim_{\epsilon \to 0} \frac{i}{2\pi} \int_{-\infty}^{+\infty} \frac{d\omega}{e^{\beta\omega}-1} \left[ G(\underline{0},\underline{0},\omega^2+i\epsilon) - G(\underline{0},\underline{0},\omega^2-i\epsilon) \right]$$

$$= \frac{1}{\pi} \int_{0}^{\infty} d\omega \coth \frac{\beta\omega}{2} \, \mathrm{Im} \, G(\underline{0},\underline{0},\omega^2-i\epsilon) \, . \quad (5.6)$$

This is the general expression. The evaluation
of the mean square displacement can be achieved in two
ways. In first method we express the $(\underline{0},\underline{0})$ element of the
perturbed Green's function in terms of the unperturbed
Green's function as has been discussed in Chapter III. An
additional term arises in this case if the denominator

vanishes outside the band producing a local mode. Then the
equation(5.6) reduces to

$$\left\langle u^2(\underline{0},0) \right\rangle = \frac{\left(1+\frac{\Delta\gamma}{\gamma}\right)^2}{\pi} \int d\omega \frac{\coth\frac{\beta\omega}{2} \, \mathrm{Img}_0}{D_R^2(\omega)+D_I^2(\omega)}$$

$$+ \frac{N(\omega_1)\coth\frac{\beta\omega_1}{2}}{\left|\frac{d}{d\omega} D_R(\omega)\right|_1} \qquad (5.7)$$

where $N(\omega_1)$ is the numerator of the $(\underline{0},\underline{0})$ element of the
perturbed Green's function. $\omega_1$ is the local mode frequency.
The first term is the contribution of all the band modes
and the second term is due to the local mode. At finite
temperature the local mode contribution is not negligible.
It has been shown[90,92] that in the presence of a local mode
a correction term to the Debye-Waller factor is to be
multiplied i.e.

$$f = e^{-K^2\left\langle u^2(\underline{0},0) \right\rangle} I_0(Z) \qquad (5.8)$$

where $I_0(Z)$ = Bessel function of imaginary argument and

$$Z = \frac{W(LM)}{\sinh(\beta\omega_1/2)} \qquad (5.9)$$

$W(LM)$ is the contribution of the local mode to the exponent
of the Debye-Waller factor at $T = 0$. At zero temperature
the correction factor reduces to unity and at higher tempe-
ratures it enhances the value of f.

The Green's functions are calculated by the method suggested by Mahanty.[134] The Debye-characteristic temperatures[135] are used for the host crystals to fit up the experimental data.[136]

The second method however is more suitable for such calculations as one need not require the computed values of the Green's function for the entire band. Using the expression for the perturbed Green's function (equation 2.51), the mean square displacement is

$$\left\langle u^2(\underline{0},0) \right\rangle = \frac{1}{4}\left(\frac{\beta}{M_0}\right) \sum_s \frac{\coth(\beta\omega_s/2)}{(\beta\omega_s/2)} \varphi'^{*}\left(\frac{0}{s}\right) \varphi'\left(\frac{0}{s}\right). \tag{5.10}$$

At high temperatures the expansion for $\coth\frac{\beta\omega_s}{2}$ in a power series is well known and is given by

$$\frac{\coth(\beta\omega_s/2)}{(\beta\omega_s/2)} = \frac{4}{(\beta\omega_s)^2} + \frac{1}{3} - \frac{1}{45}\left(\frac{\beta\omega_s}{2}\right)^2 + \frac{2}{945}\left(\frac{\beta\omega}{2}\right)^4 + \cdots$$
$$\left[\frac{\beta\omega}{2} < \pi\right] \tag{5.11}$$

Substituting equation(5.11) in equation(5.10) and making use of the closure relation as given by equation(2.40b) the mean square displacement comes out to be

$$\left\langle u^2(\underline{0},0) \right\rangle = \frac{1}{\beta M'}\left[ - M' G(\underline{0},\underline{0};0) + \frac{1}{12}\beta^2 - \frac{D(\underline{0},\underline{0})}{720}\beta^4 \right.$$
$$\left. + \frac{D^2(\underline{0},\underline{0})}{30240}\beta^6 + \cdots \right]. \tag{5.12}$$

Here only the $(\underline{0},\underline{0})$ element of the perturbed Green's function at one frequency ($\omega = 0$) enters into the calculation. Other

quantities can be calculated easily. In the scalar models the various quantities that occur in the above equation are given by

$$D(\underline{0},\underline{0}) = \frac{n\gamma}{M'} = \frac{\omega m}{2} \left( \frac{\gamma'}{\gamma} \cdot \frac{M}{M'} \right), \qquad (5.12a)$$

$$D^2(\underline{0},\underline{0}) = \frac{1}{n} \left( \frac{n\gamma'}{M'} \right)^2 \left( n + \frac{M'}{M} \right) = \frac{1}{n} \left( \frac{\omega m}{2} \right)^2 \left( \frac{M}{M'} \cdot \frac{\gamma'}{\gamma} \right)^2 \cdot$$
$$\left( n + \frac{M'}{M} \right), \qquad (5.12b)$$

and

$$G(\underline{0},\underline{0}) = g_0 + \frac{1}{n} \left( \frac{1}{\gamma} - \frac{1}{\gamma'} \right) = - \frac{1}{n} \left( \frac{x}{\gamma} + \frac{1}{\gamma'} \right). \qquad (5.12c)$$

The final expression for the mean square displacement becomes

$$\langle u^2(\underline{0},0) \rangle = \frac{k_B T}{n\gamma} \left[ x + \frac{\gamma}{\gamma'} + \frac{1}{24} \frac{M}{M'} \left( \frac{D}{T} \right)^2 - \frac{1}{2880} \frac{M}{M'} \cdot \right.$$
$$\left( \frac{M}{M'} \cdot \frac{\gamma'}{\gamma} \right) \left( \frac{D}{T} \right)^4 + \frac{1}{241920} \frac{M}{M'} \left( \frac{M}{M} \cdot \frac{\gamma'}{\gamma} \right)^2 \cdot$$
$$\left. \left( n + \frac{M'}{M} \right) \left( \frac{D}{T} \right)^6 + \dots \right]. \qquad (5.13)$$

where $k_B$ is the Boltzman constant. At high temperature this expression holds good and for many hosts the limit of temperature ( $T > \frac{\theta}{2\pi}$ ) is sufficiently low so that the Debye-Waller factor can be computed for a wide range of temperature. The value of $x$ is determined from the $(\underline{0},\underline{0})$ element of the unperturbed Green's function at $\omega = 0$.

Platinum, palladium and copper hosts were studied by Nuosbaum et al. The Green's function for a fcc structure in the scalar model are used to compute Debye-Waller factor

and to estimate the change in the nearest neighbour inter-
action. For comparison a simple cubic lattice model is also
taken as its values are readily available. These two results
together with the result of the direct expansion are tabula-
ted in Tables 2,3,4 respectively for platinum, palladium and
copper.

In case of Pt and Pd the calculation agrees fairly
well with the experiment even at high temperatures. The
direct expansion method and the result by integration method
agree reasonably at almost all temperatures except at
$T = 20^{\circ}K$ (which lies in the region where the expansion is
not valid). In fcc model the force constant change is
around 70 /. whereas the simple cubic model it is about 50 %.
However, there is a significant deviation for cu at high
temperature. This discrepancy is still retained in the
simple cubic structure.

It is seen that in this model calculation there
arises either a local mode or an inband resonant mode for
the above mass difference and force constant change para-
meters. Since the Debye-Waller factor is an integrated
effect over all the modes the presence of resonances or
localized modes in the spectrum would make it possible to
use the Einstein oscillator model as has been taken by
Nussbaum et al.

In the absence of suitable lattice models no
realistic estimation can be made, but the results are of

### Table No.2

**Debye-Waller Factor ($Fe^{57}$ in platinum host) M = 195.2amu, $\Theta_D = 225°K$**

| Temp in °K | f Nussbaum et al | Present calculation | | | | | |
|---|---|---|---|---|---|---|---|
| | | fcc | | | sc | | |
| | | (a)f ($\frac{\gamma'}{\gamma}=.33$) | Resonant or local mode $\omega/\omega_m$ | (b)f ($\frac{\gamma'}{\gamma}=.32$) | (a)f with ($\frac{\gamma'}{\gamma}=0.54$) | Resonant or local mode $\omega/\omega_m$ | (b)f with $\frac{\gamma'}{\gamma} = .58$ |
| 20 | .893 | .894 | | — | .893 | | — |
| 78 | .873 | .875 | | .885 | .871 | | .876 |
| 296 | .711 | .703 | .94 | .700 | .696 | 1.016 | .703 |
| 500 | .567 | .567 | | .552 | .535 | | .559 |
| 700 | .444 | .445 | | .447 | .445 | | .445 |

(a)  By method of integration

(b)  Direct expansion method   x = .2768  for  fcc

　　　　　　　　　　　　　　　　　　 =.489  for  sc.

## Table No. 3

Debye-Waller Factor (Fe$^{57}$ in palladium host) M = 106.2 amu, $\Theta_D$ = 270°K

| Temp in °K | f Nussbaum et al | Present calculation | | | | | |
|---|---|---|---|---|---|---|---|
| | | fcc | | | sc | | |
| | | (a)f (γ'/γ=.35) | Resonant or local mode ω/ω_m (b)f (γ'/γ=.34) | | (a)f (γ'/γ=.6) | Resonant or local mode ω/ω_m (b)f (γ'/γ=.62) | |
| 20 | .888 | .886 | — | — | .837 | — | — |
| .78 | .861 | .859 | .868 | | .859 | .859 | |
| 296 | .658 | .656 | .7 | .651 | .655 | .806 | .654 |
| 500 | .493 | .497 | .489 | | .496 | .495 | |
| 700 | .360 | .377 | .368 | | .376 | .375 | |

(a)  Method of integration

(b)  Direct expansion method    x  =  .2768  for fcc

                                   =  .489  for sc.

## Table No. 4

Debye-Waller Factor (Fe$^{57}$ in copper host) M = 63.54amu, $\Theta_D$ = 315°K

| Temp in °K | Nussbaum et al | Present calculation | | | | | |
|---|---|---|---|---|---|---|---|
| | | fcc | | | sc | | |
| | | (a)f ($\gamma$=.56) | Resonant or local mode $\omega/\omega_m$ | (b)f ($\gamma$=.52) | (a)f ($\gamma$=1.06) | Resonant or local mode $\omega/\omega_m$ | (b)f ($\gamma$=1.12) |
| 119 | .850 | .849 | | .850 | .849 | | .849 |
| 290 | .709 | .713 | | .702 | .713 | | .712 |
| 406 | .616 | .629 | .71 | .612 | .629 | .883 | .628 |
| 562 | .498 | .529 | | .509 | .530 | | .528 |
| 700 | .412 | .455 | | .426 | .455 | | .453 |

(a)   Method of integration     x = .2768   for fcc

(b)   Direct expansion method     = .489   for sc.

qualitative interest. The change of nearest neighbour
interaction is significant when the mass difference between
the host and the impurity is large, like that of $Fe^{57}$ in
Pt and Pd. But for small mass difference the anharmonic
interaction should be taken into account.

The expression for the mean square velocity which
determines the second order Doppler shift of the zero phonon
line is obtained as

$$\langle u^2_\alpha (0,0) \rangle = \frac{\beta}{M} \left[ \frac{1}{\beta^2} + \frac{1}{12} D_{\alpha\alpha} (\underline{0},\underline{0}) \right.$$

$$\left. - \frac{\beta^2}{720} D^2_{\alpha\alpha} (\underline{0},\underline{0}) + .. \right] . \quad (T > \frac{\Theta_D}{2\pi}) \quad (5.14)$$

This expression is general and the estimation of
nearest neighbour force constant can be made for any model.

CHAPTER VI

CONCLUSION

In this chapter the results obtained in the present
investigation and their limitations are briefly discussed.

The expressions derived for power absorption due
to a substitutional impurity and the total integrated absorp-
tion are general for harmonic crystal possessing a first
order electric dipole moment. The absorption line-shapes
are evaluated theoretically in detail for charged impurities
in otherwise uncharged host lattices (simple cubic, body-
centered cubic and face-centered cubic) and for mixed alkali
halides (diatomic simple cubic lattice with alternate +ve and
-ve charges) for scalar models, with the hope that the exact
solutions in these idealised models would give some insight
to the real problem.

The group theoretic method clearly reveals the
symmetry mode vibrations of the defect and its surrounding
atoms which are affected. Out of all the symmetry modes of
vibrations possible in the crystal only one mode namely the
s-wave vibration becomes infrared active. The inband reso-
nances occuring in this branch have been fitted to the exper-
imental data obtained from the infrared absorption in alkali
halides. The tremendous softening of nearest neighbour force
constant especially for small ions like $Li^{6,7}$ in KBr suggests
the departure of impurity potential from that of the harmonic
approximation. As has been discussed in chapter IV the

potential inside the cavity has a multiwell shape for small ions and quantum mechanical description of tunnelling motion is reasonably adequate to describe its dynamics. However, the interaction of such an atom with the rest of the crystal should be taken into account for a better analysis.

Using the experimental values for the Debye-Waller factor of $Fe^{57}$ in Pt, Pd and Cu an estimate of the impurity-host force constant is made.

All the results obtained are more or less qualitative, because any quantitative estimation should take into account the realistic features of the lattice i.e. the true density of states for the host crystal. The formalism used is very general. Further study can be made by using a polarization model for the host lattice within the same theoretical frame work as presented here, but it involves far more elaborate calculations and numerical computations. Besides, the theory should incorporate anharmonicity, higher order electric moments and long range interactions between atoms for a complete description. The later interaction is of importance in case of ionic crystals.

The electric field $\underline{E}$ of the electromagnetic radiation should be replaced by an effective field (or local field) $\underline{E}_{loc}$ inside the dielectric material, which takes into account the polarization of the medium. This brings into the picture the dielectric constant of the crystal and the intensity of the source as parameters.

## Appendix I

The vibration of an impurity atom is related to the perturbed Green's function of the lattice. As indicated in equation(3.16), the perturbed Green's function $G(\underline{0},\underline{0},\omega^2-i\epsilon)$ which determines the vibrations of the impurity and hence the infrared absorption, equals $[(\hat{I}+\hat{g}\,\hat{p})\hat{g}]_{\underline{0},\underline{0}}$. The matrices $\hat{g}$, $\hat{p}$ and hence $(\hat{I}+\hat{g}\,\hat{p})\hat{g}$ can be block-diagonalized by a unitary matrix $\hat{V}$ into submatrices belonging to different irreducible representations of the point group that occurs in the reducible representation generated by the affected lattice sites (equation 3.18). Denoting the block-diagonal form of $(\hat{I}+\hat{g}\,\hat{p})\hat{g}$ by $\hat{B}$, we have,

$$\hat{B} = \hat{V}^{+}(\hat{I}+\hat{g}\,\hat{p})^{-1}\hat{g}\,\hat{V} \qquad\qquad \text{(A-1)}$$

$$= \begin{pmatrix} B_1 & 0 & 0 & .. \\ 0 & B_2 & 0 & .. \\ 0 & 0 & B_3 & .. \\ . & . & . & .. \end{pmatrix} = \begin{pmatrix} B_1 & 0 & 0 & .. \\ 0 & 0 & 0 & .. \\ . & . & . & .. \\ . & . & . & .. \end{pmatrix} + \begin{bmatrix} 0 & 0 & 0 & .. \\ 0 & B_2 & 0 & .. \\ . & . & . & .. \\ . & . & . & .. \end{bmatrix} + \cdots$$

$$= \sum_{\mu} \hat{M}_{\mu}. \qquad\qquad \text{(A-2)}$$

From equation (A-1) we obtain,

$$(\hat{I}+\hat{g}\,\hat{p})\hat{g} = \hat{V}\,\hat{B}\,\hat{V}^{+} = \sum_{\mu} \hat{V}\,\hat{M}_{\mu}\,\hat{V}^{+}, \qquad\qquad \text{(A-3)}$$

where each term on the right side of equation(A-3) belongs to a distinct irreducible representation. The $(\underline{0},\underline{0})$ element

of $\hat{G}$ now becomes

$$G\ (\underline{0},\underline{0},\omega^2-i\varepsilon) = \sum_{\mu}' (\hat{V}\ \hat{M}_\mu\hat{V}^+)_{\underline{0},\underline{0}} \ . \qquad (A-4)$$

The $\hat{V}$ matrix is constructed as follows. The vector defined by,

$$\psi' \ = \ \begin{pmatrix} X(0) \\ X(1) \\ \cdot \\ \cdot \\ X(n) \end{pmatrix} \qquad (A-5)$$

generates a reducible representation $\Gamma$ which can be reduced as,

$$\Gamma = \sum_{\mu}' a_\mu \Gamma^{(\mu)} \qquad (A-6)$$

where $a_\mu$ denotes the number of times the irreducible representation $\Gamma^{(\mu)}$ occurs in $\Gamma$. If $\Gamma^{(\mu)}$ is $n_\mu$-dimensional, the matrices $D^{(\mu)}_{(R)}$ for the operation $O_R$ (corresponding to the group element R) will have $n_\mu$ columns and rows. Then the columns of the unitary matrix $\hat{V}$, which are orthonormalized vectors, can be projected out of $\psi$ by the projection operator, in the form

$$\psi^{(\mu)} \ = \ \frac{n_\mu}{g} \sum_R \ D^{(\mu)}_{ii}(R)O_R \ . \qquad (A-7)$$

where g is the order of the group and the index runs from 1 to $n_\mu$. Thus the columns of $\hat{V}$ divide into sets of $n_\mu$ vectors

for each $\Gamma^{(\mu)}$ and the members of the set are labelled by the index i.

In our notation the indices of the first element of the perturbation matrix $\hat{P}$ correspond to the impurity site. The elements of the first row of the $\hat{V}$ matrix which are given by $\psi_i^{(\mu)}(0)$ for various values of $\mu$ and i can be evaluated trivially, noting that all operations $O_R$ of the group leave the first element $X(0)$ of $\psi$ unchanged. Therefore,

$$\psi_i^{(\mu)}(0) = \frac{n_\mu}{g} \sum_R' D_{ii}^{(\mu)}(R) \ X(0)$$

$$= \frac{n_\mu X(0)}{g} \sum_R' D_{ii}^{(\mu)}(R) \ . \qquad (A-8)$$

However, from the orthogonality relations for the matrix elements of different irreducible representations it follows that

$$\sum_R' D_{ii}^{(\mu)}(R) = 0 \ . \qquad\qquad (A-9)$$

for every $\mu$, except the totally symmetric one-dimensional representation, for which we get,

$$\frac{1}{g} \sum_R' D^{(1)}(R)_{11} = 1 \ . \qquad\qquad (A-10)$$

Thus all the elements of the first row of $\hat{V}$ are zero except the first one, which is unity. From the unitarity of $\hat{V}$

matrix it follows that the elements of the first column (except the first element) are also zero. Hence we get

$$G(\underline{0},\underline{0},\omega^2-\varepsilon) = \sideset{}{'}\sum_{\mu} (\hat{V}\ \dot{M}_{\mu}\ \hat{V}^{T})_{\underline{0},\underline{0}}$$

$$= \sideset{}{'}\sum_{\mu,\underline{n},\underline{m}} \hat{V}(\underline{0},\underline{n})\ \hat{M}_{\mu}(\underline{n},\underline{m})\hat{V}^{+}(\underline{m},\underline{0})$$

$$= \sideset{}{'}\sum_{\mu} \hat{M}_{\mu}(\underline{0},\underline{0}) \qquad (A\text{-}11)$$

The only $\hat{M}_{\mu}$ which has non-vanishing $(\underline{0},\underline{0})$ - element is the one that is generated by the columns in $\hat{V}$ matrix corresponding to the totally symmetric irreducible representation. Hence it follows that the block corresponding to the totally symmetric or s-wave representation contributes to the impurity vibration.

The explicit form of $\hat{V}$ matrices are given below

(i) Simple cubic lattice

$$\hat{V}_{S} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & a & d & 0 & 0 & c & e \\ 0 & a & 0 & d & 0 & c & -e \\ 0 & a & 0 & 0 & d & -2c & 0 \\ 0 & a & -d & 0 & 0 & c & e \\ 0 & a & 0 & -d & 0 & c & -e \\ 0 & a & 0 & 0 & -d & -2c & 0 \end{pmatrix} \qquad (A\text{-}12)$$

$$\underbrace{\hphantom{1\quad 0}}_{2A_{1g}}\quad \underbrace{\hphantom{0\ \ 0\ \ 0}}_{F_{1u}}\quad \underbrace{\hphantom{c\ \ \ e}}_{E_{g}}$$

(ii) Body-Centered cubic lattice

$$
\hat{V}_B = 
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & b & b & b & b & b & b & b & b \\
0 & b & b & -b & b & b & -b & -b & -b \\
0 & b & -b & -b & b & -b & -b & b & b \\
0 & b & -b & b & b & -b & b & -b & -b \\
0 & b & -b & -b & -b & b & b & b & -b \\
0 & b & -b & b & -b & b & -b & -b & b \\
0 & b & b & b & -b & -b & -b & b & -b \\
0 & b & b & -b & -b & -b & b & -b & b
\end{pmatrix}
$$

$\underbrace{\quad}_{2A_{1g}} \quad \underbrace{\qquad}_{F_{1u}} \quad \underbrace{\qquad}_{F_{2g}} \quad \underbrace{\quad}_{A_{2u}}$

(iii) Face-centered cubic lattice

$$
\hat{V}_F = 
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & c & b & 0 & b & b & h & e & 0 & 0 & b & b & 0 \\
0 & c & b & 0 & -b & b & h & -e & 0 & 0 & -b & b & 0 \\
0 & c & b & b & 0 & 0 & -2h & 0 & e & 0 & 0 & -b & b \\
0 & c & b & -b & 0 & 0 & -2h & 0 & -e & 0 & 0 & -b & -b \\
0 & c & 0 & b & -b & -b & h & 0 & 0 & e & b & 0 & -b \\
0 & c & 0 & b & b & -b & h & 0 & 0 & -e & -b & 0 & -b \\
0 & c & -b & 0 & -b & b & h & e & 0 & 0 & -b & -b & 0 \\
0 & c & -b & 0 & b & b & h & -e & 0 & 0 & b & -b & 0 \\
0 & c & -b & -b & 0 & 0 & -2h & 0 & e & 0 & 0 & b & -b \\
0 & c & -b & b & 0 & 0 & -2h & 0 & -e & 0 & 0 & b & b \\
0 & c & 0 & -b & b & -b & h & 0 & 0 & e & -b & 0 & b \\
0 & c & 0 & -b & -b & -b & h & 0 & 0 & -e & b & 0 & b
\end{pmatrix}
$$

$\underbrace{\quad}_{2A_{1g}} \quad \underbrace{\qquad}_{F_{1u}} \quad \underbrace{\qquad}_{E_g} \quad \underbrace{\qquad}_{F_{2g}} \quad \underbrace{\qquad}_{F_{2u}}$ (A-14)

Here

$$a = \frac{1}{\sqrt{6}} \quad , \quad b = \frac{1}{\sqrt{8}} \quad , \quad c = \frac{1}{\sqrt{12}} \quad ,$$

$$d = \frac{1}{\sqrt{2}} \quad , \quad e = \frac{1}{2} \quad , \quad h = \frac{1}{\sqrt{24}} \quad .$$

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